

Supporting Information
Asymmetric Total Synthesis of Bioactive Natural Lipid Mycalol

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- 1. General Experimental Procedure: S2**
- 2. NMR Comparison Tables: S(2-8)**
- 3. HPLC Data for mixture of compound 15a and 15b: S9**
- 4. Copies of Spectra: S(10-84)**

General Experimental Procedure:

All moisture sensitive reactions were performed in oven or flame-dried glassware with Teflon coated magnetic stirring bar under argon atmosphere using dry, freshly distilled solvents, unless otherwise noted. Air- and moisture-sensitive liquids were transferred via a gastight syringe and a stainless-steel needle. Reactions were monitored by thin layer chromatography (TLC, Silica gel 60 F₂₅₄) plates with UV light, ethanolic anisaldehyde (with 1% AcOH and 3.3% conc. H₂SO₄)-heat and aqueous KMnO₄ (with K₂CO₃ and 10% aqueous NaOH solution) as developing agents. All workup and purification procedures were carried out with reagent-grade solvents under ambient atmosphere unless otherwise stated. Column chromatography was performed using silica gel 60-120 mesh and 100-200 mesh. Yields mentioned as chromatographically and spectroscopically homogeneous materials unless otherwise stated. Optical rotations were measured using sodium (589, D line) lamp and are reported as follows: $[\alpha]_D^{25}$ (c = mg/100 ml, solvent). IR spectra were recorded as thin films (for liquids). HRMS were taken using Quadruple-TOF (Q-TOF) micro MS system using electrospray ionisation (ESI) technique. ¹H NMR spectra were recorded on 300 and 500 MHz spectrometers in appropriate solvents and calibrated using residual undeuterated solvent as an internal reference, and the chemical shifts are shown in δ ppm scales. Multiplicities of NMR signals are designated as s (singlet), d (doublet), t (triplet), q (quartet), br s (broad singlet), m (multiplet, for unresolved lines) etc. ¹³C spectra were recorded on 75, 100 and 125 MHz spectrometers.

Table 1: ^{13}C NMR comparison of mycalol (natural, $\text{C}_5\text{D}_5\text{N}$, 600 MHz), compound 1 ($\text{C}_5\text{D}_5\text{N}$, 300 MHz) δ in ppm.

Natural Mycalol	Compound 1
170.7	170.7
75.9	75.9
75.3,75.3	75.3
74.3	74.3
73.8	73.9
73.0	72.7
72.0	71.9
69.7	69.7
64.7	64.7
34.5,34.5	34.5,34.2
33.6,33.6	33.6
32.0	Merged with other signals
30.7	30.6
30.4	30.4
30.0,30.0,30.0,30.0	30.3,30.1,29.9,29.9,29.9,
29.8,29.8	29.8,27.8
26.7	26.8
25.7	25.7
25.3	Merged with other signals
22.8	22.8
21.1	21.1
14.1	14.1

Table 2: ^{13}C NMR comparison of triacetone (natural, CDCl_3 , 600 MHz), compounds 21, 22, 23, 24 (CDCl_3 , 300 MHz) δ in ppm.

Natural triacetone	Compound 21	Compound 22	Compound 23	Compound 24
171.0	171.1	171.1	171.1	171.1
109.4	109.6	109.6	109.6	109.5
107.6	107.8	107.8	107.8	107.8
107.4	107.5	107.6	107.6	107.5
78.3	78.5	78.2	78.2	78.5
78.2	78.4	74.9	77.6	78.4
78.1	78.2	74.8	74.9	78.2
74.8	74.9	74.8	74.8	74.9
74.6	74.9	74.6	74.6	74.6
74.5	74.6	Merged with other signals	Merged with other signals	Merged with other signals
71.9	72.3	72.3	72.3	72.1
68.7	68.8	68.9	68.9	68.8
66.9	67.0	66.9	66.9	67.0
34.1	34.3	34.3	34.3	34.3
34.0	33.9	33.9	33.9	33.9
31.7	Merged with other signals	32.1	Merged with other signals	Merged with other signals
30.2	30.3	30.2	30.2	30.3
29.7	29.8,29.7	29.8	29.8,29.8,29.7	29.8
29.5	29.1	29.8,29.7	29.5	29.7,29.7
28.6	28.7	28.7	28.7	28.8,28.7
27.2	27.6,27.2	27.6	28.7	27.6
26.8	26.9	26.9	27.8	27.3
26.4	26.5	26.6,26.5	26.6	26.9
26.0	26.1	26.2	26.2	26.5
25.9	26.1	26.1	26.1,26.1	26.1
25.4	25.5	25.6	25.6	25.6
25.3	25.5	25.5	25.5	25.5
25.0	Merged with other signals	Merged with other signals	Merged with other signals	Merged with other signals
22.5	22.7	22.8	22.8	22.8
21.3	21.4	21.4	21.4	21.4
14.1	14.1	14.1	14.1	14.1

Table 3: ^{13}C NMR comparison of triacetonide (natural, CDCl_3 , 600 MHz), compounds 43, 44, 45, 46 (CDCl_3 , 300 MHz) δ in ppm.

Natural triacetonide	Compound 43	Compound 44	Compound 45	Compound 46
171.0	171.1	171.1	171.1	171.1
109.4	109.5	109.5	109.5	109.6
107.6	107.8	107.8	107.8	107.7
107.4	107.6	107.6	107.5	107.5
78.3	78.5	78.2	78.5	78.5
78.2	78.3	Merged with other signals	78.4	78.4
78.1	78.2	Merged with other signals	78.2	78.2
74.8	74.8	75.0	75.0	74.9
74.6	74.6	74.8	74.8	74.9
74.5	74.5	74.6	74.6	Merged with other signals
71.9	72.1	72.1	72.1	72.6
68.7	68.8	68.9	68.9	68.8
66.9	67.0	66.9	67.0	67.0
34.1	34.3	34.3	34.3	34.3
34.0	33.9	33.9	33.9	33.9
31.7	Merged with other signals	32.1	Merged with other signals	Merged with other signals
30.2	30.3	30.2	30.3	30.3
29.7	29.8,29.7,29.7	29.9,29.8,29.7	29.8	29.8,29.8,29.8
29.5	29.5	29.5	29.8	29.7,29.5
28.6	28.7	28.7	28.7	28.8
27.2	27.6	27.6	27.6	27.3
26.8	26.9	26.9	27.3	26.9
26.4	26.5	26.6	27.2	26.5
26.0	26.1	26.4		26.1
25.9	26.0	26.1	26.1	26.1
25.4	25.6	25.6	25.5	25.6
25.3	25.5	25.5	25.5	25.5
25.0	Merged with other signals	Merged with other signals	Merged with other signals	Merged with other signals
22.5	22.8	22.8	22.8	22.7
21.3	21.4	21.4	21.4	21.4
14.1	14.1	14.1	14.1	14.1

Table 4: ^{13}C NMR comparison of triacetonide (natural, CDCl_3 , 600 MHz), compounds 53, 54 (CDCl_3 , 300 MHz) δ in ppm.

Natural triacetonide	Compound 53	Compound 54
171.0	171.1	171.1
109.4	109.6	109.6
107.6	107.7	107.7
107.4	107.5	107.4
78.3	78.2	78.2
78.2	77.8	78.1
78.1	77.8	77.9
74.8	74.9	74.9
74.6	74.8	74.8
74.5	74.6	74.6
71.9	72.2	72.6
68.7	68.9	68.8
66.9	66.9	66.9
34.1	34.3	34.3
34.0	33.9	33.9
31.7	32.1	Merged with other signals
30.2	30.3	30.3
29.7	29.8	29.8
29.5	29.7,29.5	29.7,29.7
28.6	28.7	28.8
27.2	27.6	27.6
26.8	26.9	26.9
26.4	26.4	26.6
26.0	26.2	26.6
25.9	26.1	26.1
25.4	25.6	25.6
25.3	25.5	25.5
25.0	Merged with other signals	Merged with other signals
22.5	22.8	22.8
21.3	21.5	21.4
14.1	14.1	14.1

Table 5: ^{13}C NMR comparison of triacetonide (natural, CDCl_3 , 600 MHz), compounds 65, 66 (CDCl_3 , 300 MHz) δ in ppm.

Natural triacetonide	Compound 65	Compound 66
171.0	171.1	171.1
109.4	109.6	109.5
107.6	107.8	107.8
107.4	107.5	107.5
78.3	78.5	78.5
78.2	78.3	78.4
78.1	78.2	78.2
74.8	74.9	74.9
74.6	74.8	74.8
74.5	74.6	74.6
71.9	72.3	72.1
68.7	68.8	68.8
66.9	67.0	67.0
34.1	34.3	34.3
34.0	Merged with other signals	34.2
31.7	31.9	31.9
30.2	30.3	30.3
29.7	29.8,29.7	29.8
29.5	29.3	29.7
28.6	28.7	28.7
27.2	27.3	27.2
26.8	26.9	26.9
26.4	26.5	26.5
26.0	26.1	26.1
25.9	25.9	25.9
25.4	25.5	25.6
25.3	25.4	25.5
25.0	Merged with other signals	25.1
22.5	22.7	22.7
21.3	21.4	21.4
14.1	14.2	14.1

Table 6: ^1H and ^{13}C NMR comparison of mycalol (natural, $\text{C}_5\text{D}_5\text{N}$, 600 MHz), compound 2 ($\text{C}_5\text{D}_5\text{N}$, 300 MHz) δ in ppm.

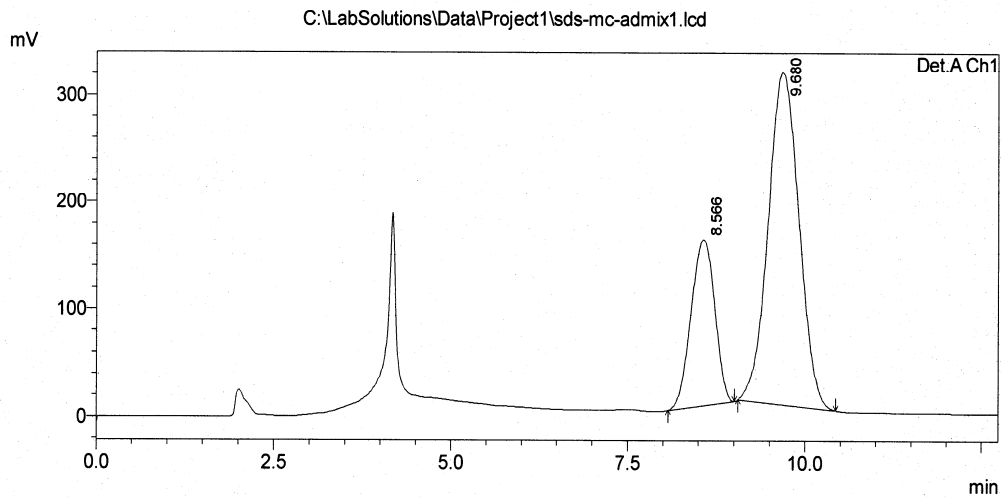
^1H NMR of Natural Mycalol	^1H NMR of Compound 2	^{13}C NMR of Natural Mycalol	^{13}C NMR of Compound 2
5.07, m, 1H	5.13-5.05, m, 1H (Merged with water signal)	170.7	170.7
4.35, m, 1H	4.38-4.34, m, 1H	75.9	75.9
4.18, m, 1H	4.24-4.18, m, 1H	75.3,75.3	75.2
4.08, m, 2H 4.06, m, 1H 4.05, m, 1H	4.14-4.07, m, 4H	74.3	74.2
3.99, m, 1H 3.97, m, 2H	4.04-3.94, m, 3H	73.8	73.7
3.90, <i>dd</i> , 9.5, 5.0 Hz, 1H 3.85, <i>dd</i> , 9.5, 6.0 Hz, 1H	3.93-3.82, m, 2H	73.0	72.9
2.59, <i>bd</i> , 8.2 Hz, 2H	2.57, <i>bd</i> , 9.3 Hz, 2H	72.0	71.9
2.40, m, 1H	2.41-2.35, m, 1H	69.7	69.6
2.16, m, 1H 2.11, m, 2H 2.09, s, 3H	2.18-2.09, m, 6H	64.7	64.7
1.99, m, 1H 1.87, m, 1H 1.86, m, 1H	1.98-1.79, m, 3H	34.5,34.5	34.5,34.4
1.56, m, 5H	1.58-1.50, m, 5H	33.6,33.6	33.6
1.40-1.26, m, 8H 1.36, m, 2H 1.33, m, 4H 1.22, m, 4H 1.20, m, 2H	1.34-1.21, m, 20H	32.0	31.9
0.82, <i>t</i> , 6.7 Hz, 3H	0.81, <i>t</i> , 6.9 Hz, 3H	30.7	30.6
		30.4	30.3
		30.0,30.0,30.0,30.0	30.0,29.8
		29.8,29.8	29.8,29.8
		26.7	26.7
		25.7	25.7
		25.3	25.3
		22.8	22.7
		21.1	21.1
		14.1	14.1

HPLC Data for mixture of compound 15a and 15b:

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\sds-mc-admix1.lcd
 Acquired by : Admin
 Sample Name : sds-mc-admix
 Sample ID : sds-mc-admix
 Vial # : 1
 Injection Volume : 15 uL
 Data File Name : sds-mc-admix1.lcd
 Method File Name : HEX-IPA 95-5 40 min.lcm
 Batch File Name : SingleRun120141014223818.lcb
 Report File Name : Default.lcr
 Data Acquired : 10/14/2014 10:39:01 PM
 Data Processed : 10/22/2014 10:04:25 AM

<Chromatogram>



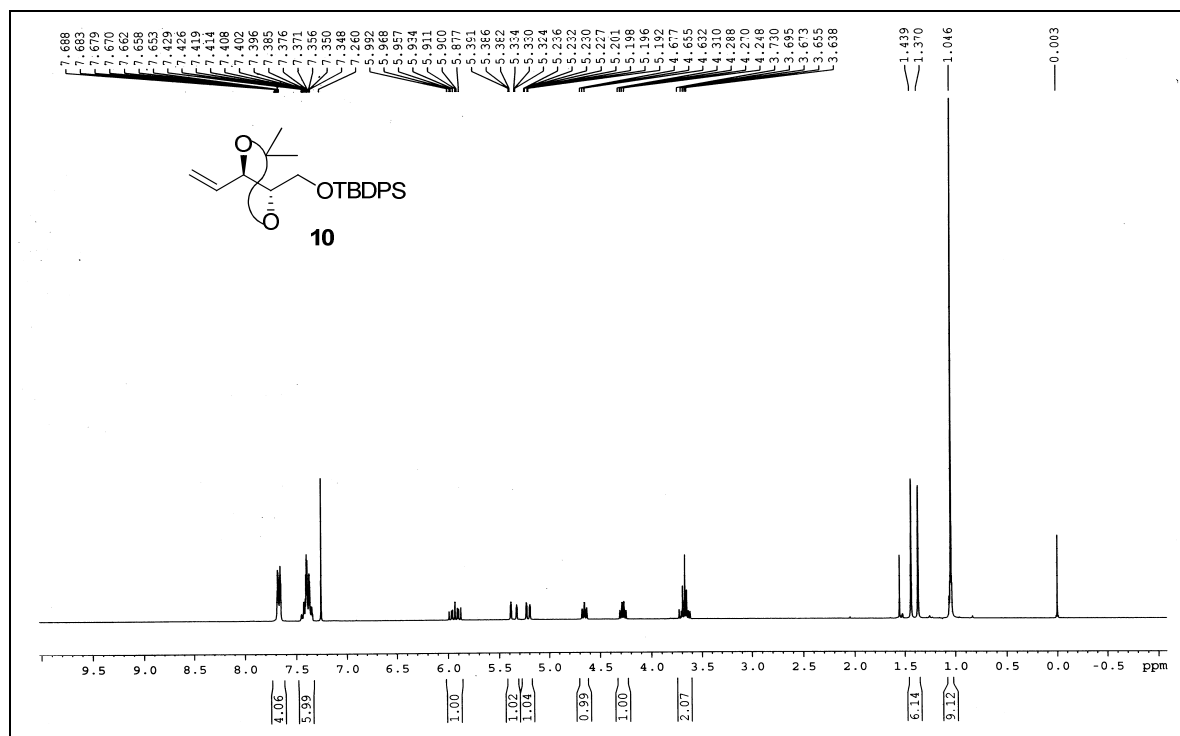
PeakTable

Detector A Ch1 254nm

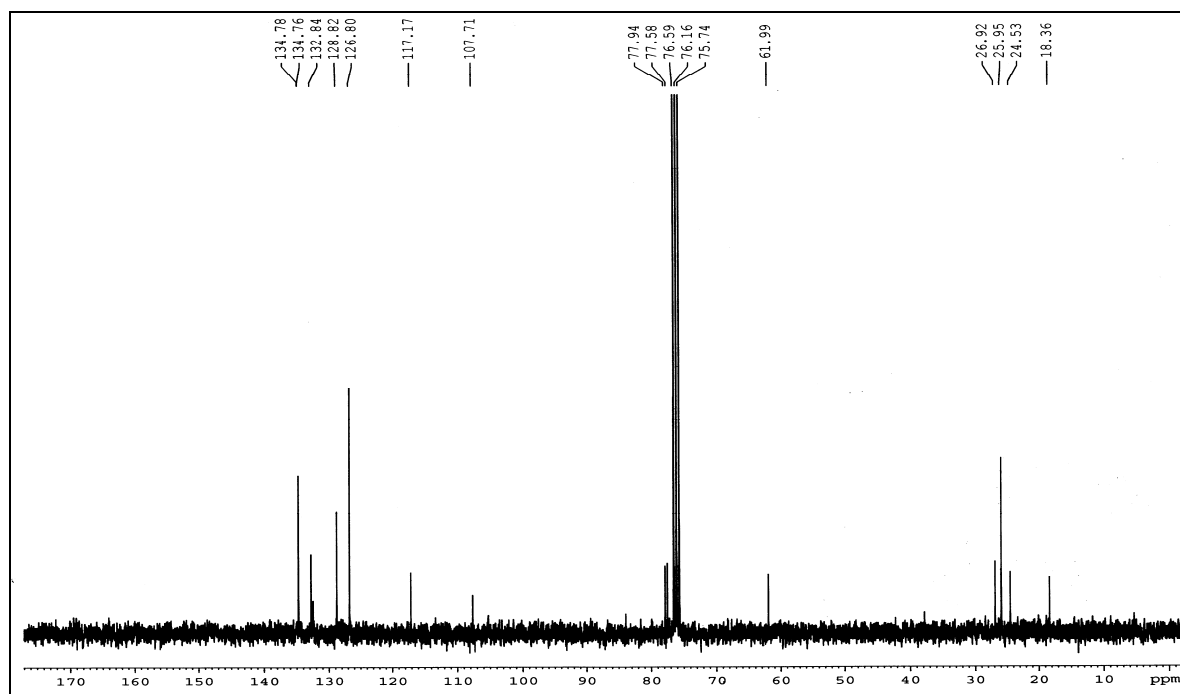
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.566	3585291	154645	27.750	33.282
2	9.680	9334643	310008	72.250	66.718
Total		12919934	464653	100.000	100.000

Spectra (^1H NMR, ^{13}C NMR, HRMS) of compounds:

^1H NMR spectrum of 10 (300 MHz, CDCl_3):



^{13}C NMR spectrum of 10 (75 MHz, CDCl_3):



CC(C)(OCC1C(C(C(C1)OC(C)(C)C)OC(C)(C)C)OC(C)(C)C)OC(C)(C)C

11

δ (ppm): 7.619, 7.613, 7.608, 7.603, 7.653, 7.653, 7.643, 7.643, 7.637, 7.637, 7.487, 7.458, 7.453, 7.441, 7.441, 7.436, 7.420, 7.413, 7.405, 7.388, 7.388, 7.388, 7.388, 7.379, 7.369, 7.353, 7.339, 7.240, 4.414, 4.395, 4.388, 4.378, 4.369, 4.350, 4.350, 4.242, 4.213, 4.213, 4.216, 4.193, 3.874, 3.874, 3.857, 3.837, 3.818, 3.818, 3.732, 3.723, 3.723, 3.697, 3.678, 3.662, 3.662, 3.627, 2.316, 1.932, 1.932, 1.914, 1.904, 1.904, 1.882, 1.882, 1.855, 1.355, 1.332, 1.030, 0.011, -0.100.

Integration: 4.02, 5.33, 1.00, 1.02, 2.17, 2.06, 0.93, 1.96, 2.94, 2.22, 2.27.

135.70
133.31
133.19
129.97
127.92
127.91

108.32

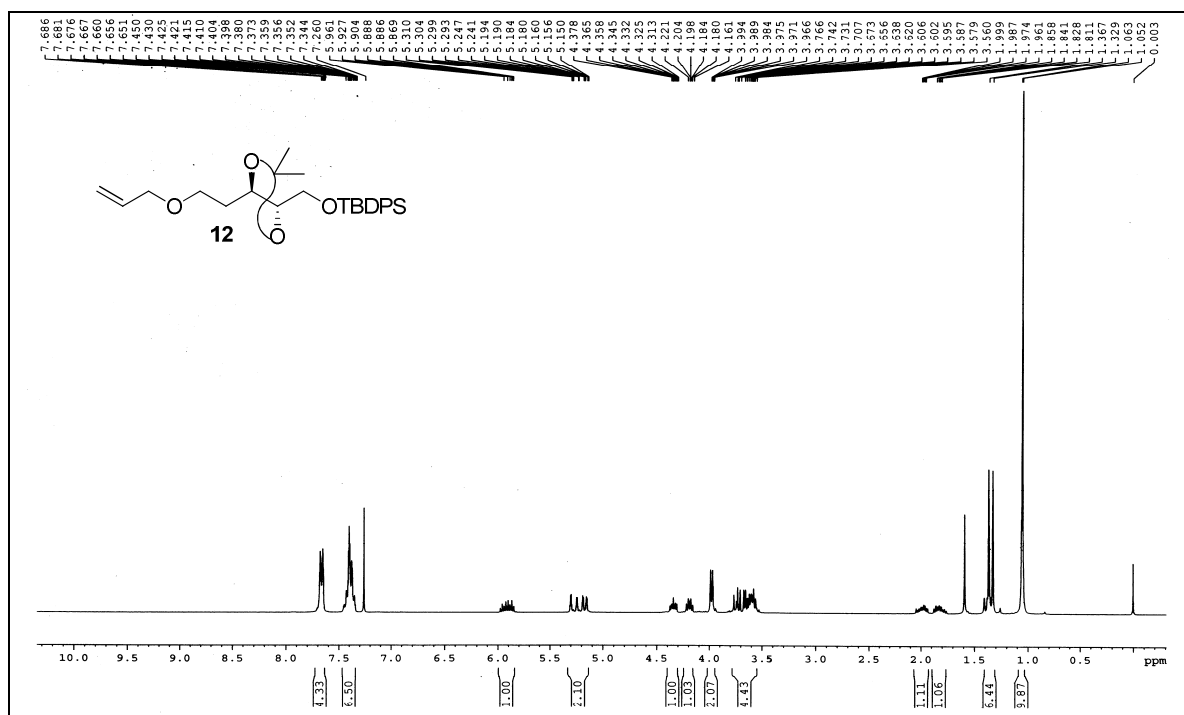
77.86
77.58
77.16
16.74

62.65
61.65

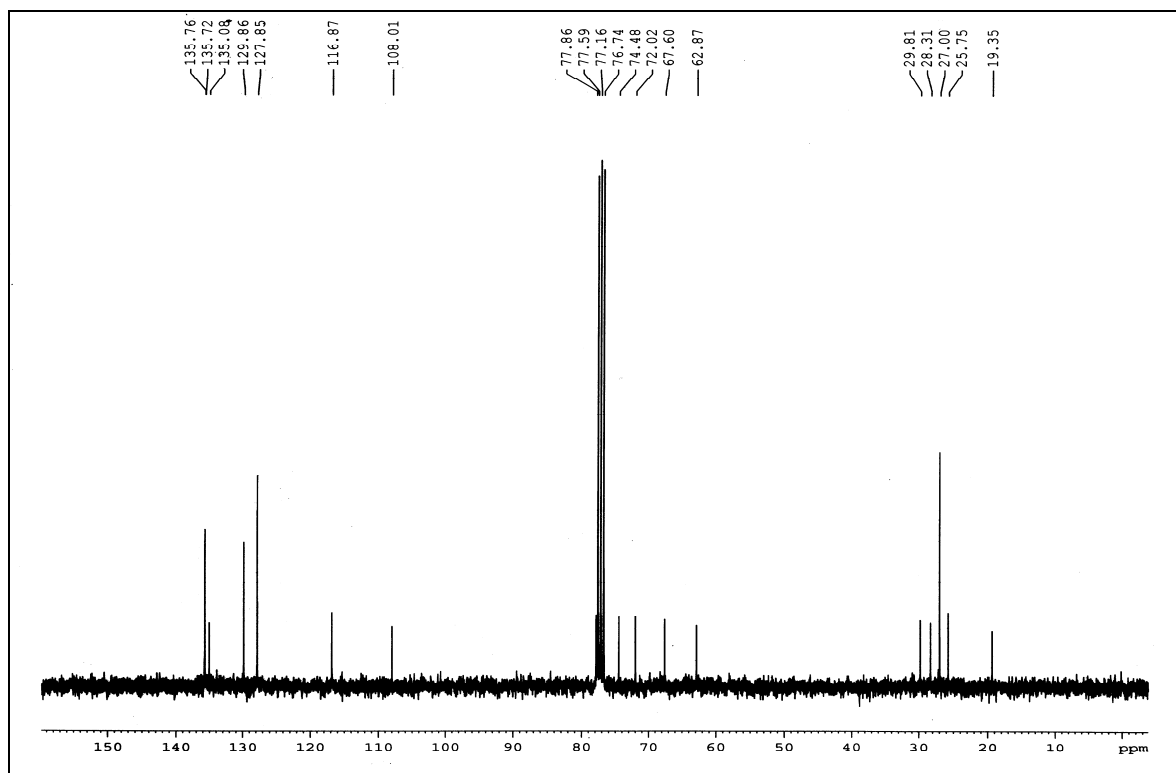
31.64
28.19
26.98
25.67
19.32

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

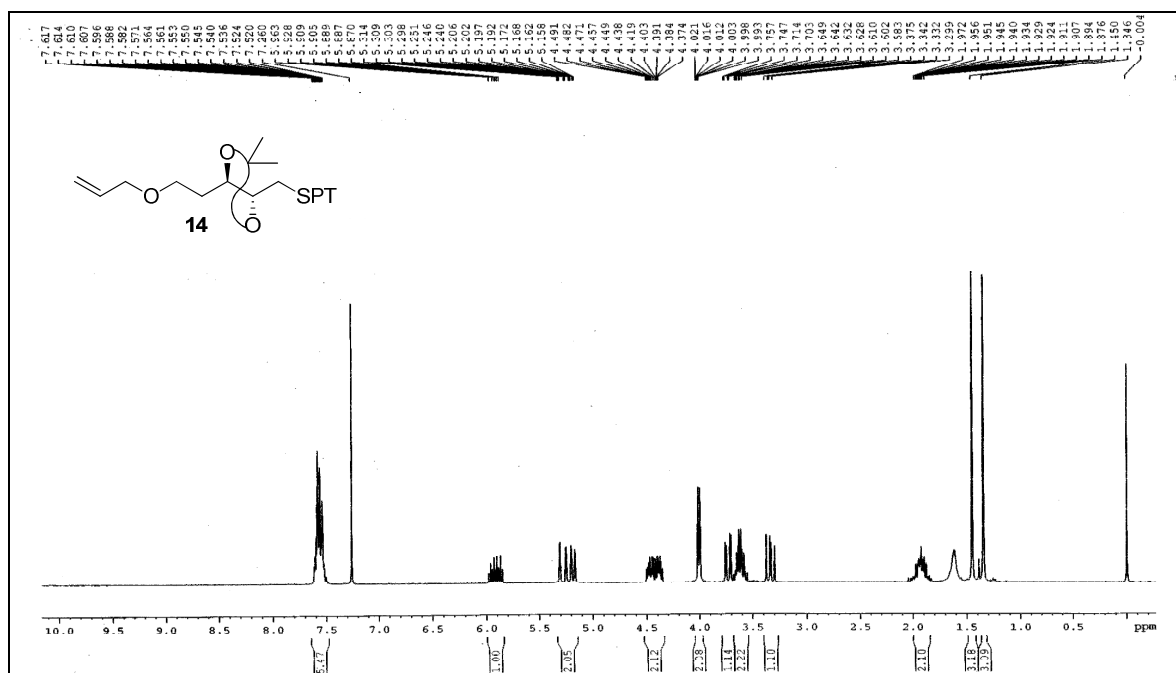
^1H NMR spectrum of 12 (300 MHz, CDCl_3):



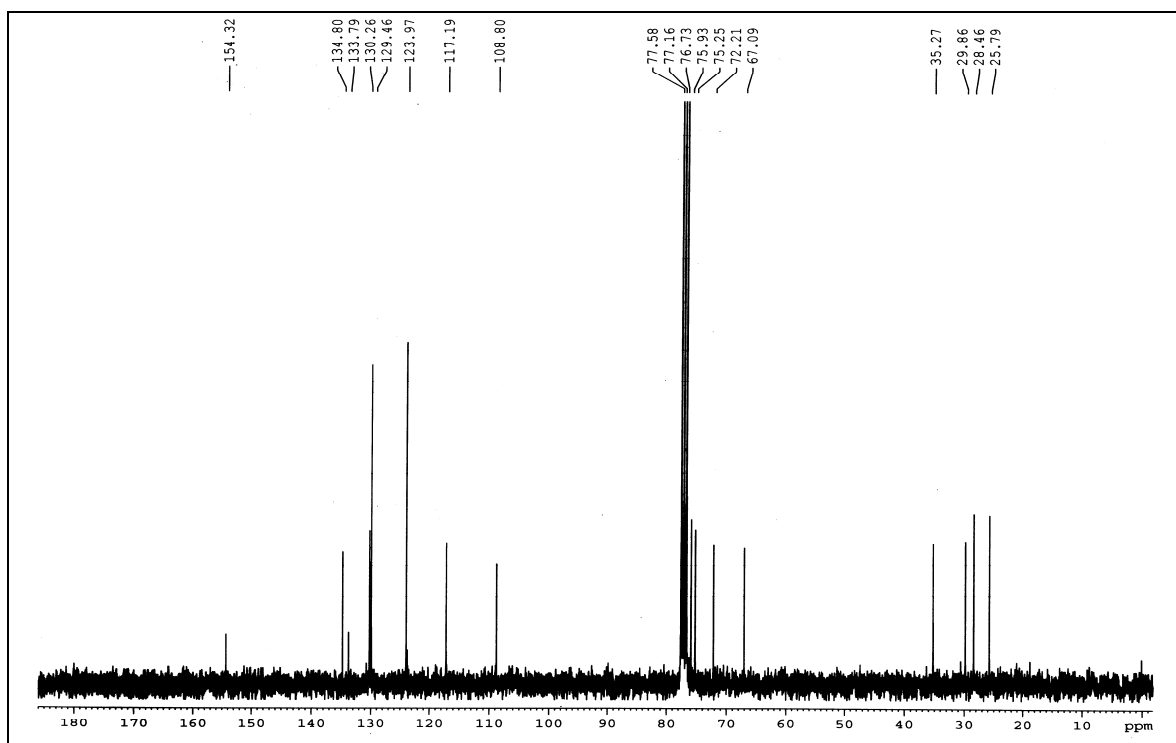
^{13}C NMR spectrum of 12 (75 MHz, CDCl_3):



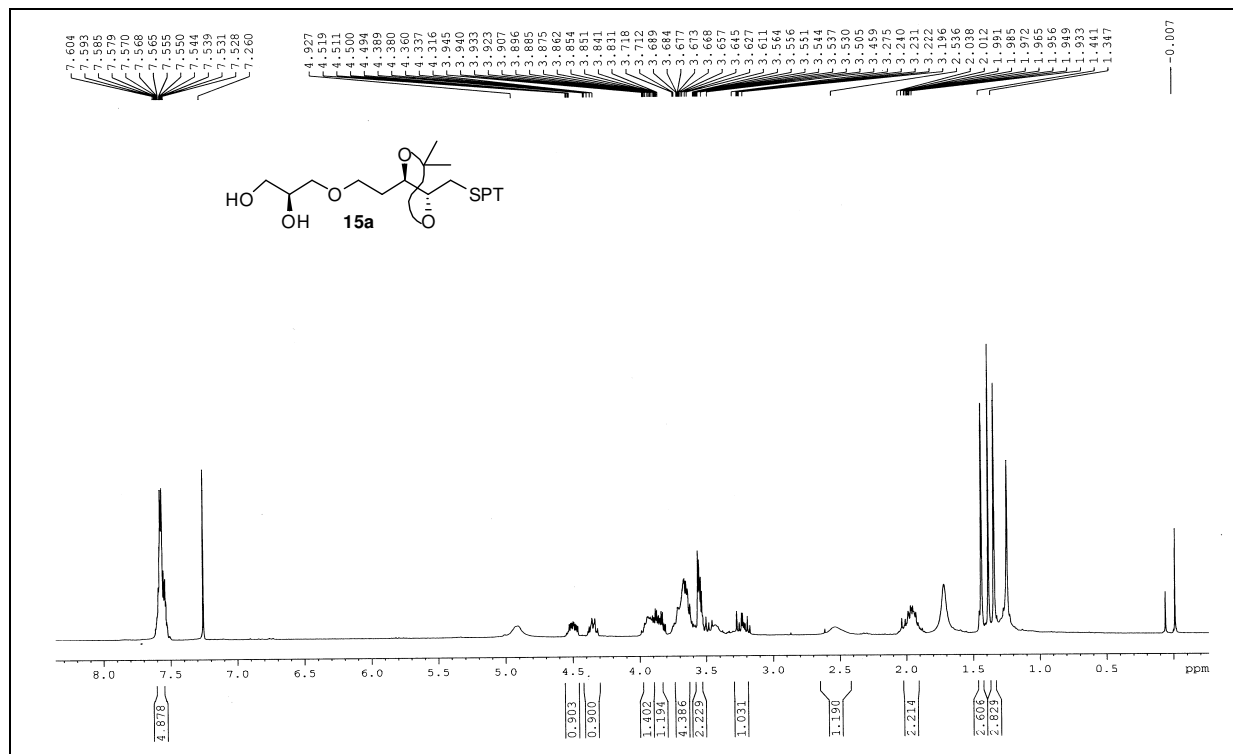
^1H NMR spectrum of 14 (300 MHz, CDCl_3):



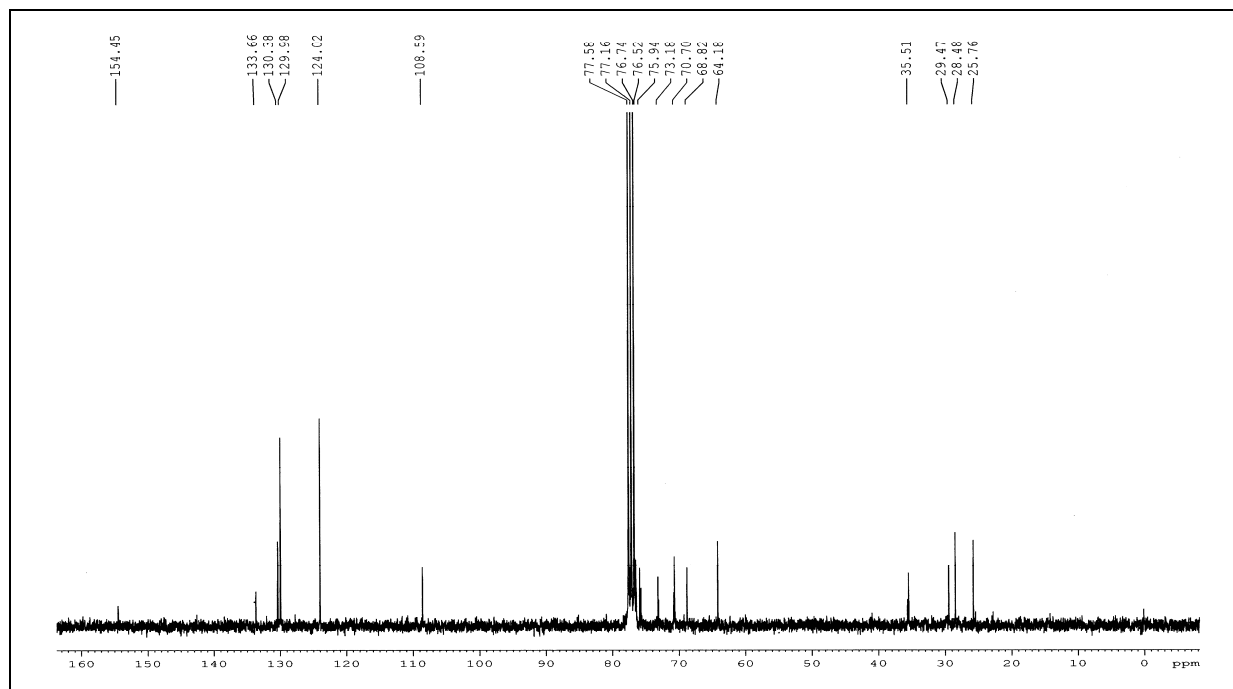
^{13}C NMR spectrum of 14 (75 MHz, CDCl_3):



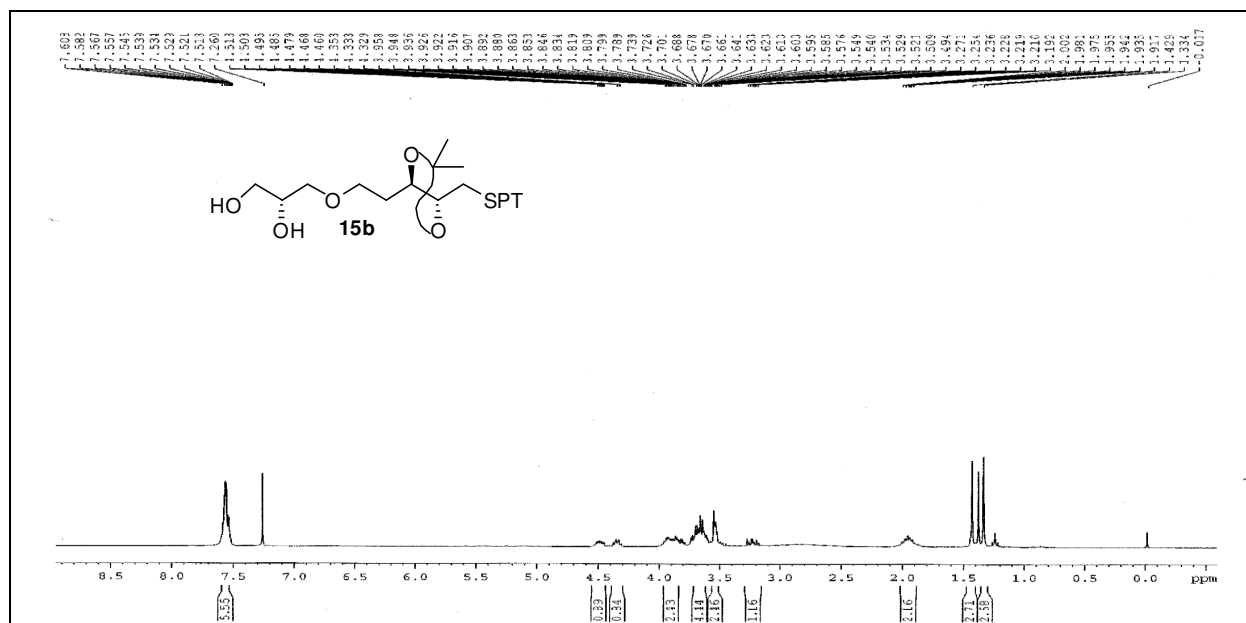
^1H NMR spectrum of 15a (300 MHz, CDCl_3):



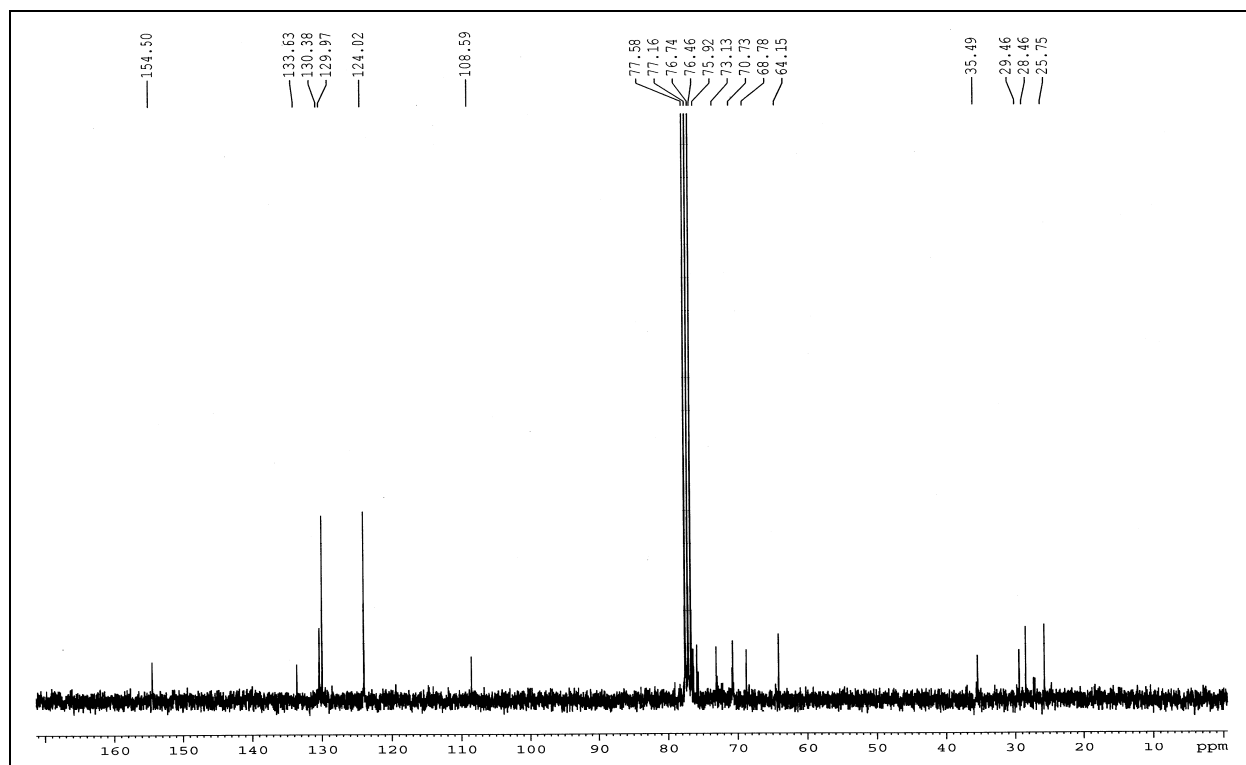
^{13}C NMR spectrum of 15a (75 MHz, CDCl_3):



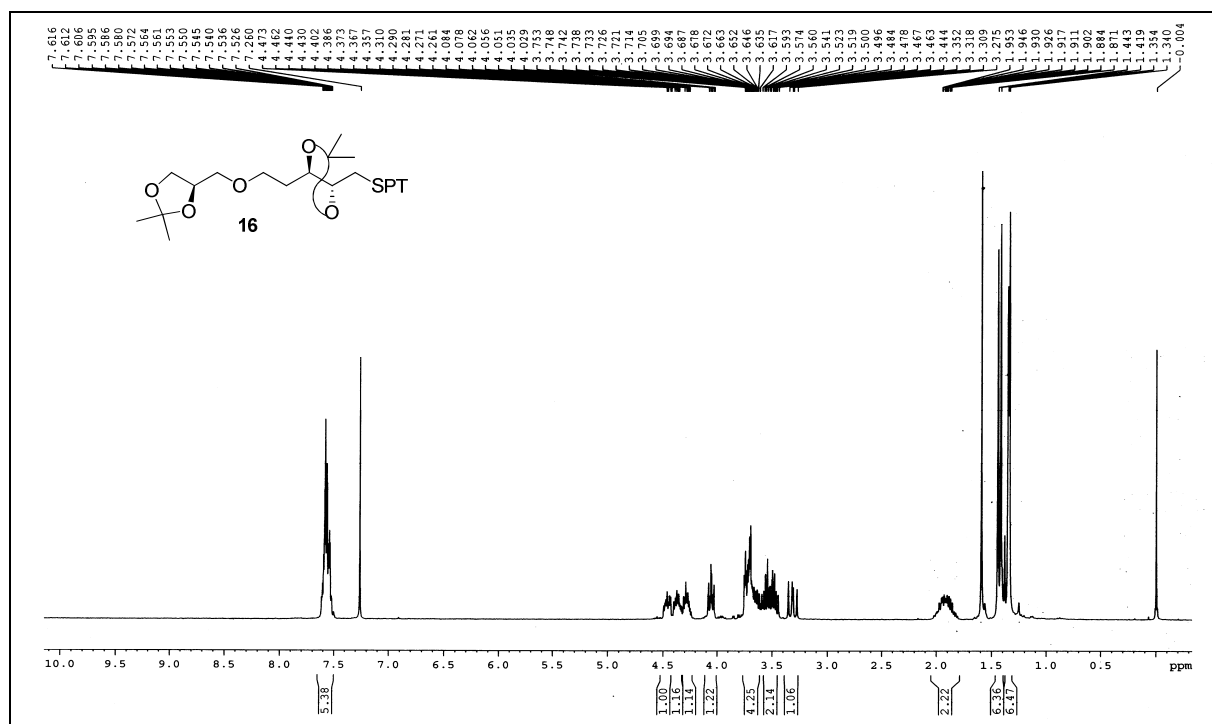
^1H NMR spectrum of 15b (300 MHz, CDCl_3):



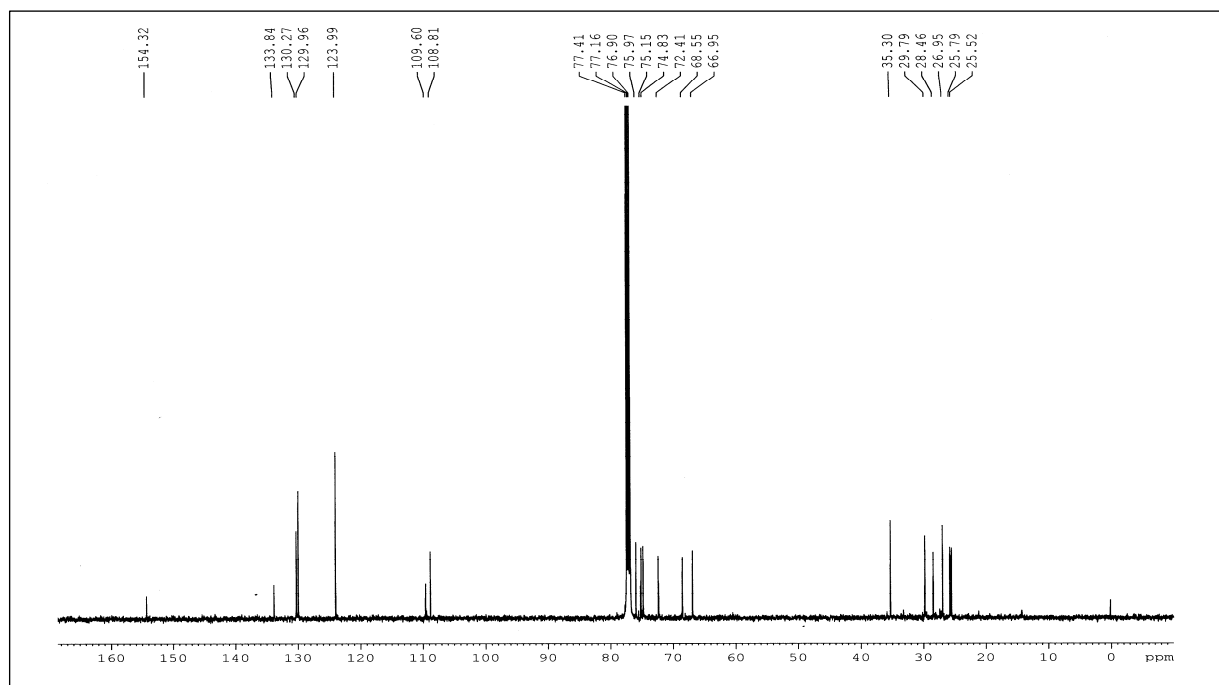
^{13}C NMR spectrum of 15b (125 MHz, CDCl_3):



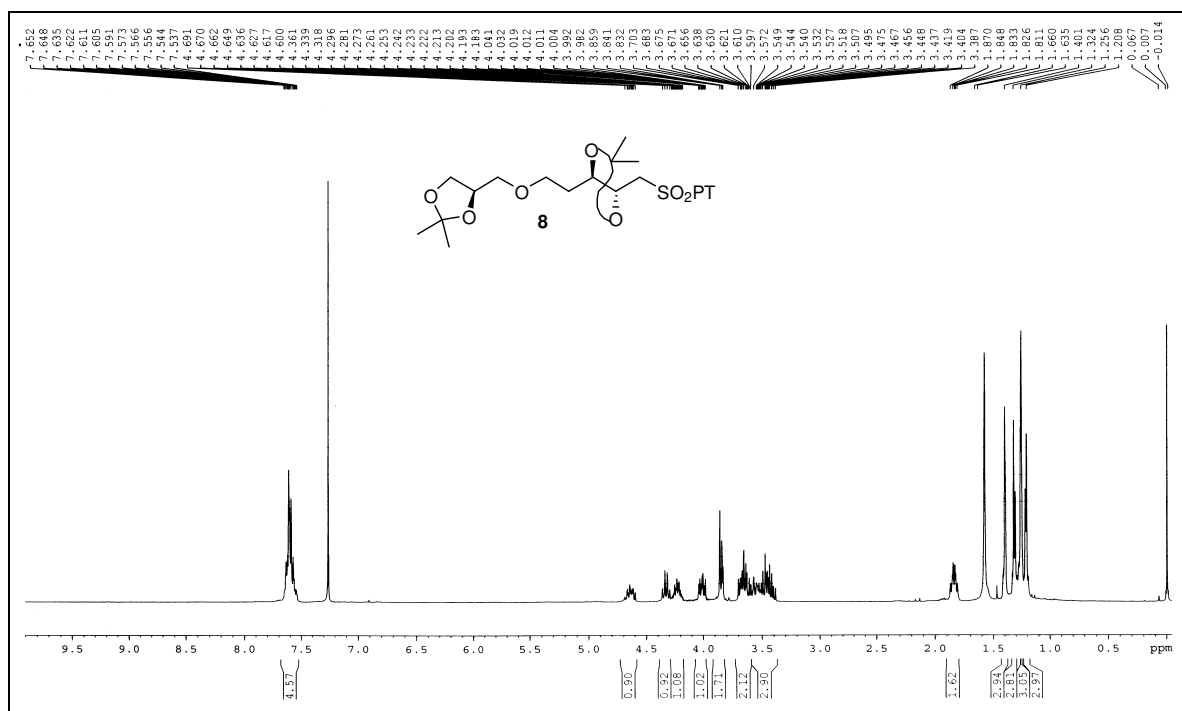
^1H NMR spectrum of 16 (300 MHz, CDCl_3):



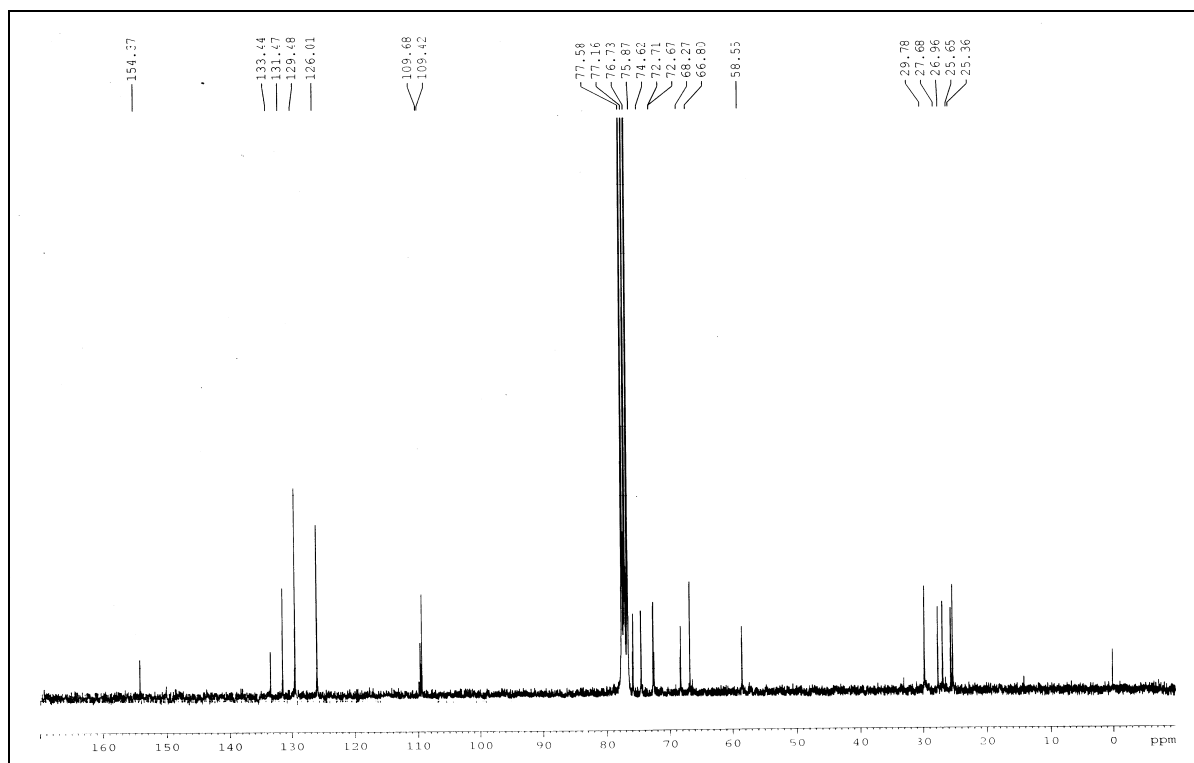
^{13}C NMR spectrum of 16 (125 MHz, CDCl_3):



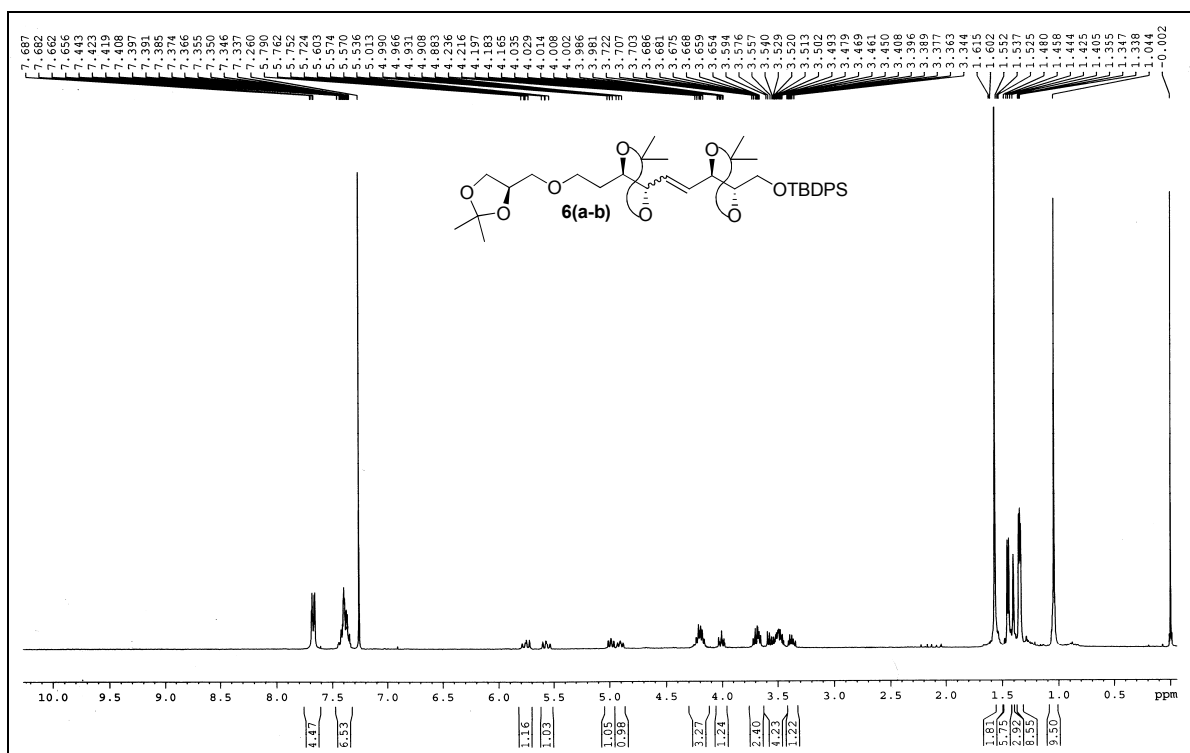
^1H NMR spectrum of 8 (300 MHz, CDCl_3):



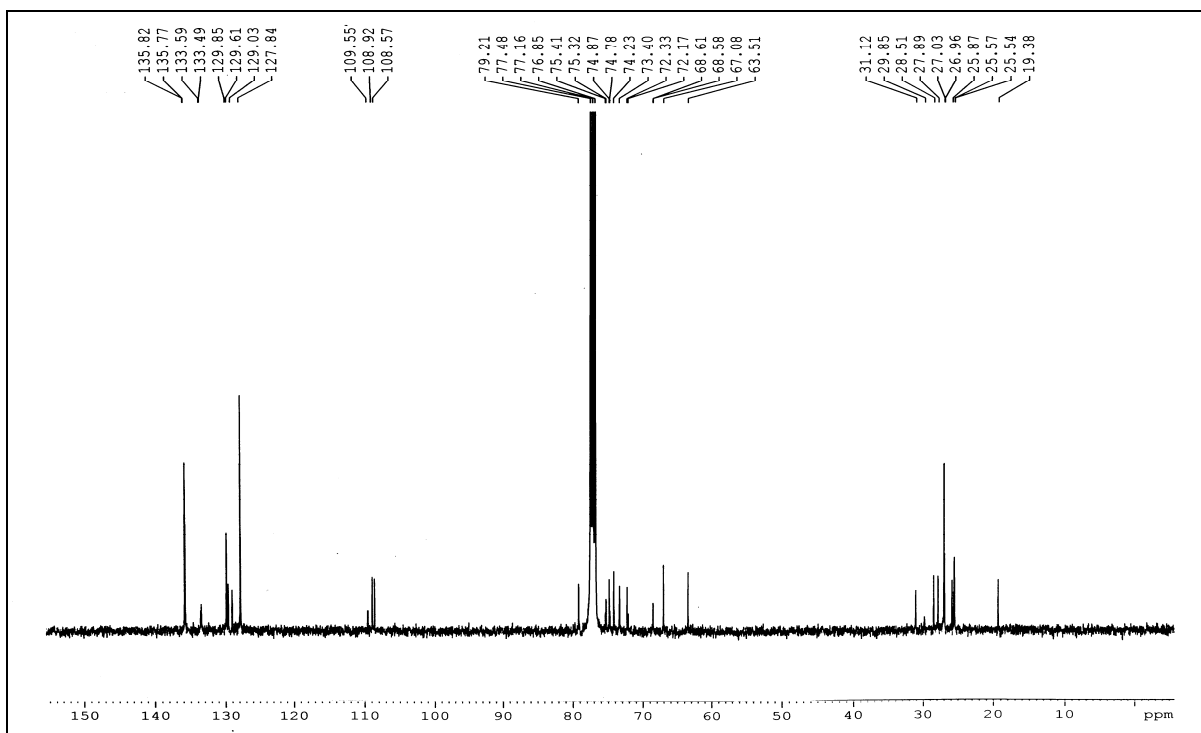
^{13}C NMR spectrum of 8 (75 MHz, CDCl_3):



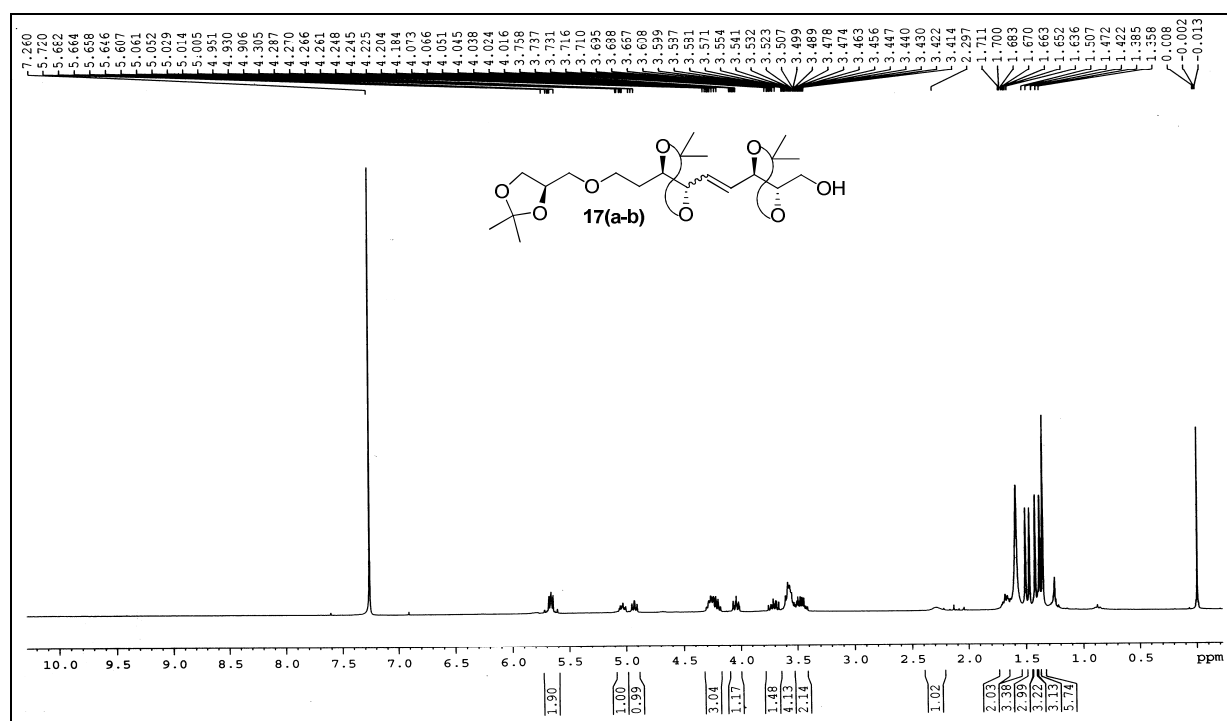
^1H NMR spectrum of diastereomeric mixture of 6(a-b) (300 MHz, CDCl_3):



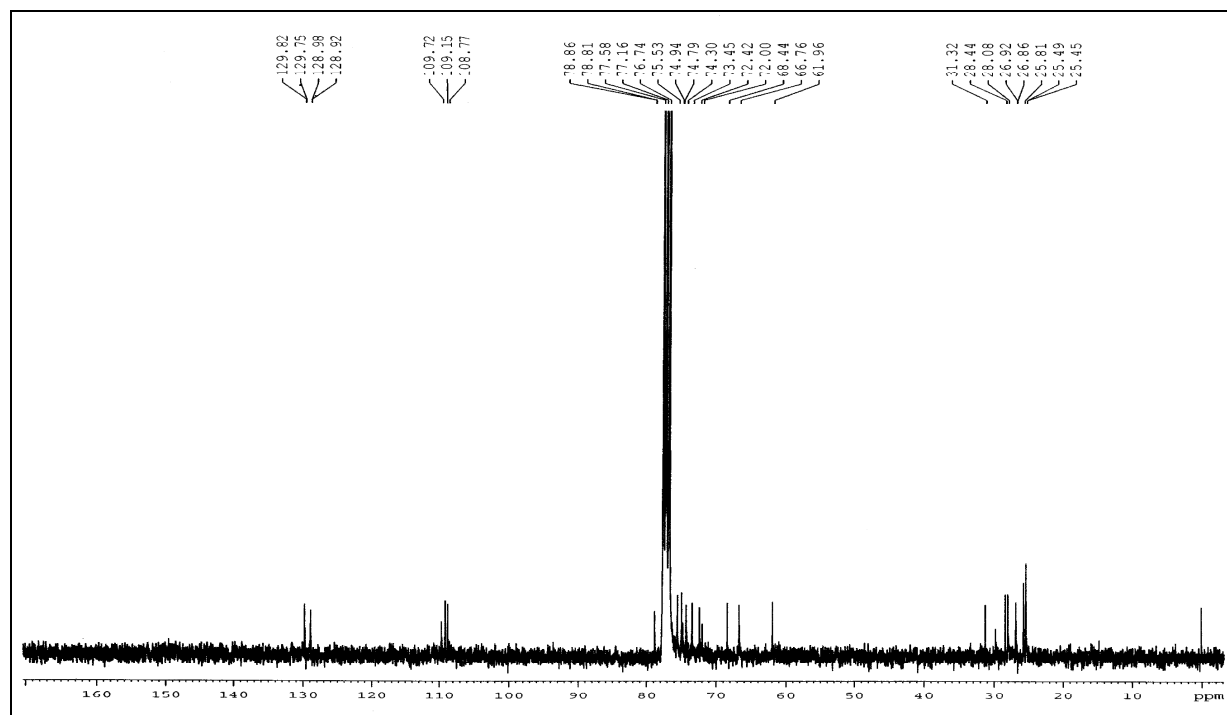
^{13}C NMR spectrum of diastereomeric mixture of 6(a-b) (75 MHz, CDCl_3):



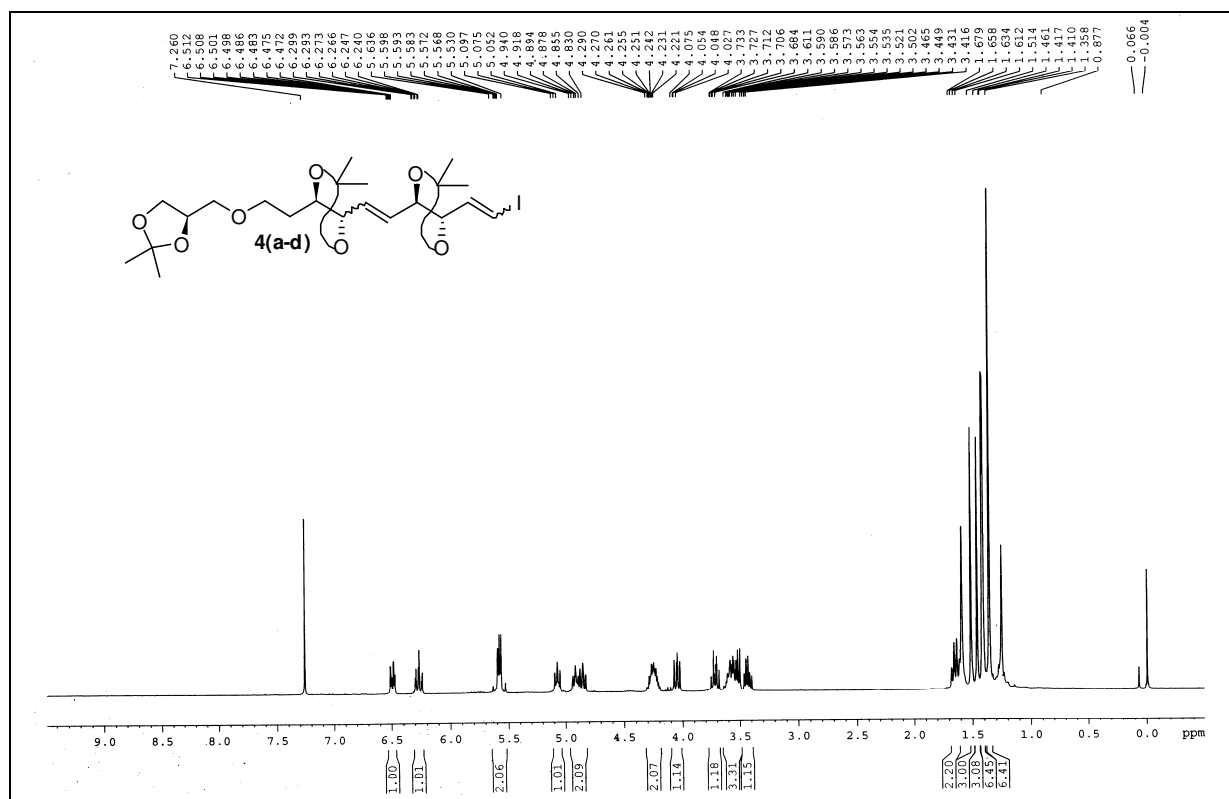
¹H NMR spectrum of diastereomeric mixture of 17(a-b) (300 MHz, CDCl₃):



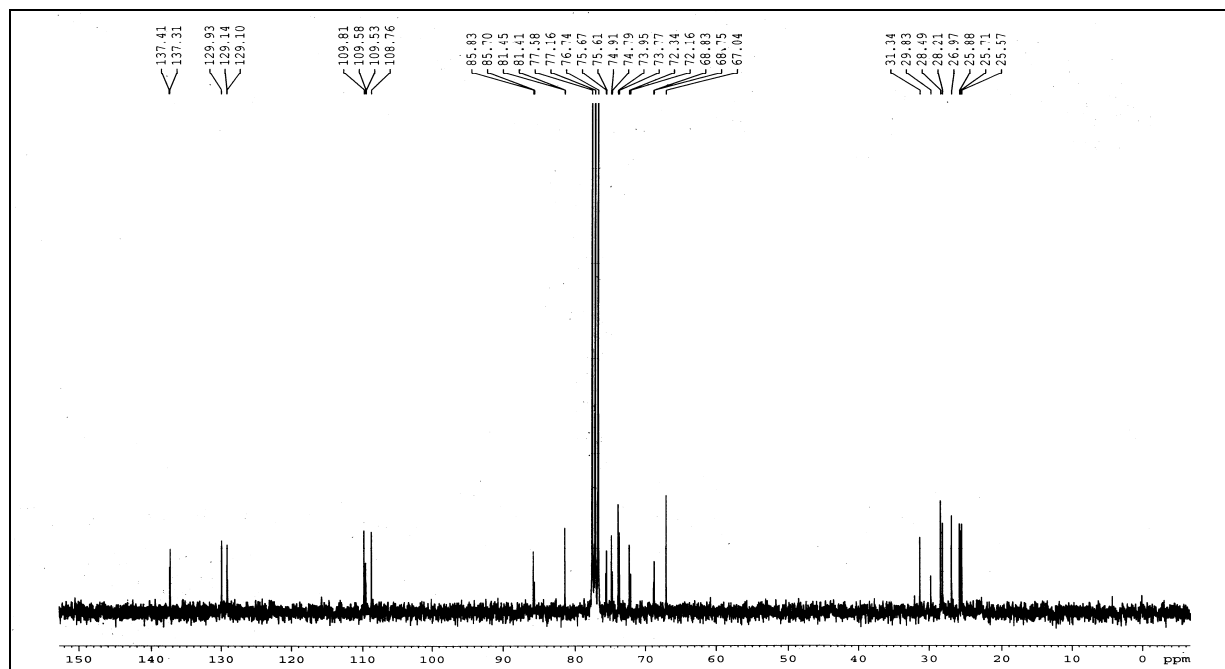
¹³C NMR spectrum of diastereomeric mixture of 17(a-b) (75 MHz, CDCl₃):



^1H NMR spectrum of diastereomeric mixture of 4(a-d) (300 MHz, CDCl_3):



^{13}C NMR spectrum of diastereomeric mixture of 4(a-d) (75 MHz, CDCl_3):



CCCC[C@H](O)CC#CCCC

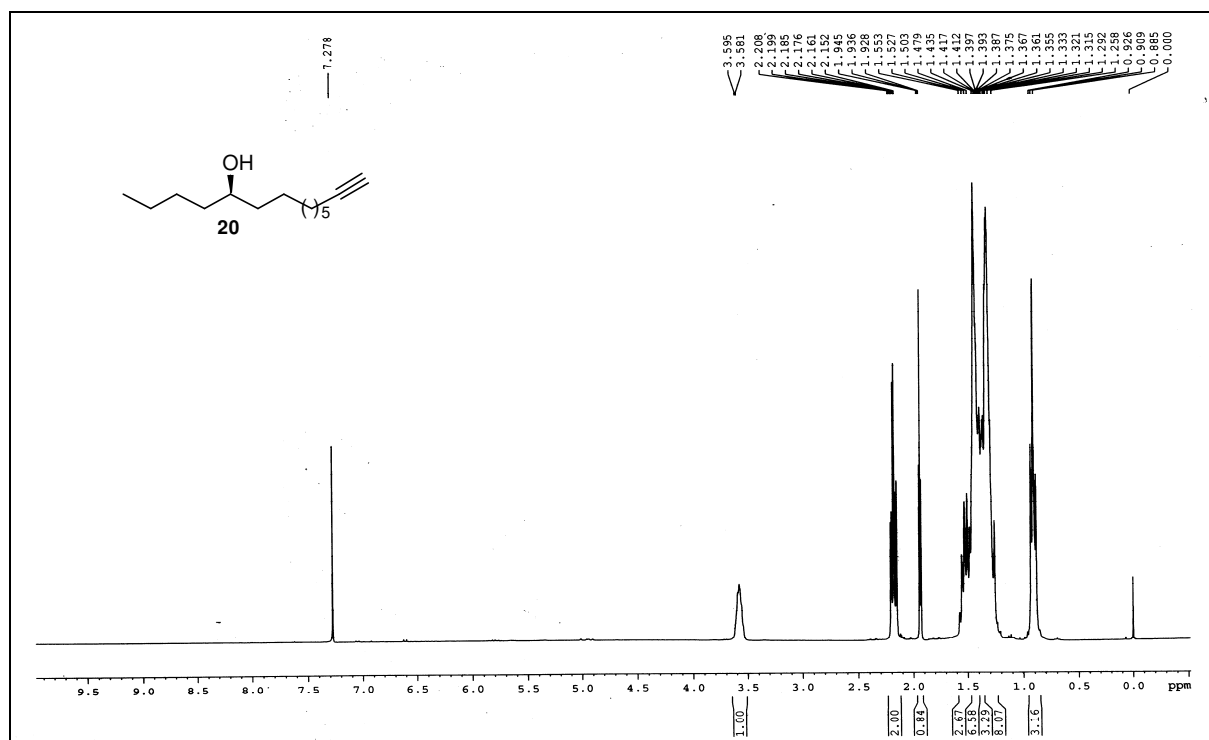
19

1.00
 1.06
 1.08
 2.09
 0.91
 4.39
 10.74
 6.15

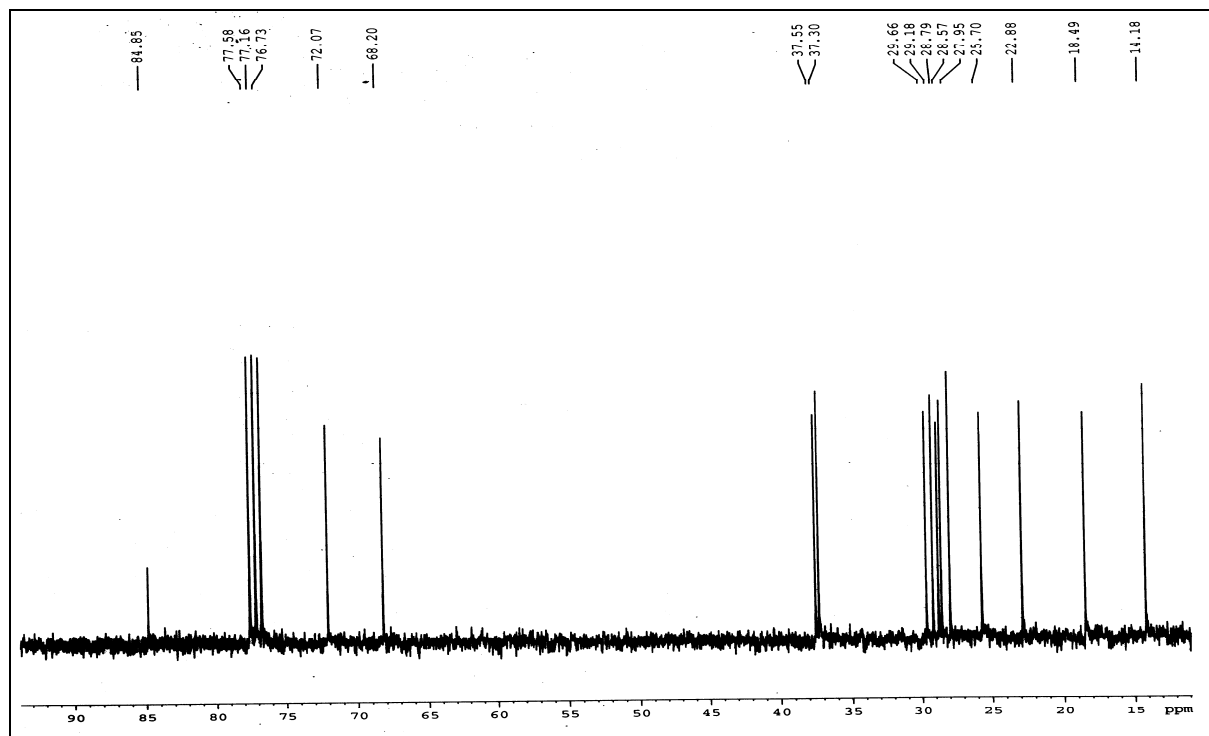
3.672
 3.661
 2.408
 2.404
 2.399
 2.395
 2.391
 2.371
 2.367
 2.362
 2.357
 2.352
 2.279
 2.275
 2.269
 2.265
 2.261
 2.256
 2.246
 2.241
 2.237
 2.232
 2.228
 2.220
 2.170
 2.166
 2.156
 2.152
 2.148
 2.143
 2.138
 1.988
 1.511
 1.496
 1.489
 1.484
 1.474
 1.459
 1.454
 1.430
 1.418
 1.413
 1.396
 1.389
 1.375
 1.360
 1.351
 1.345
 1.341
 1.341
 1.327
 1.312
 1.304
 1.303
 1.290
 1.276
 1.267
 1.254
 1.245
 1.231
 0.909
 0.895
 0.888
 0.881
 0.875

13C NMR spectrum (CDCl₃) of compound 1. The spectrum shows peaks at the following chemical shifts (ppm): 83.37, 77.48, 77.16, 76.84, 76.24, 70.37, 36.07, 31.47, 29.11, 28.69, 27.95, 27.91, 22.78, 22.67, 18.88, and 14.13.

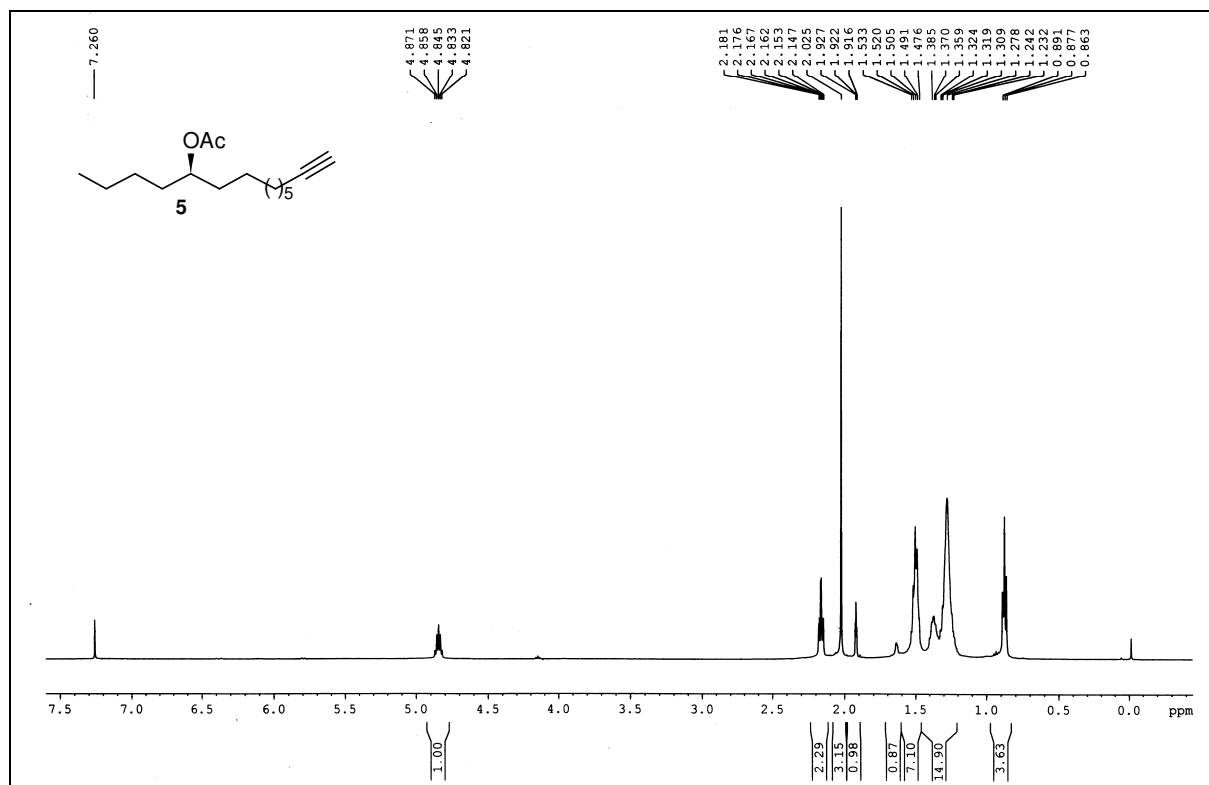
¹H NMR spectrum of 20 (300 MHz, CDCl₃):



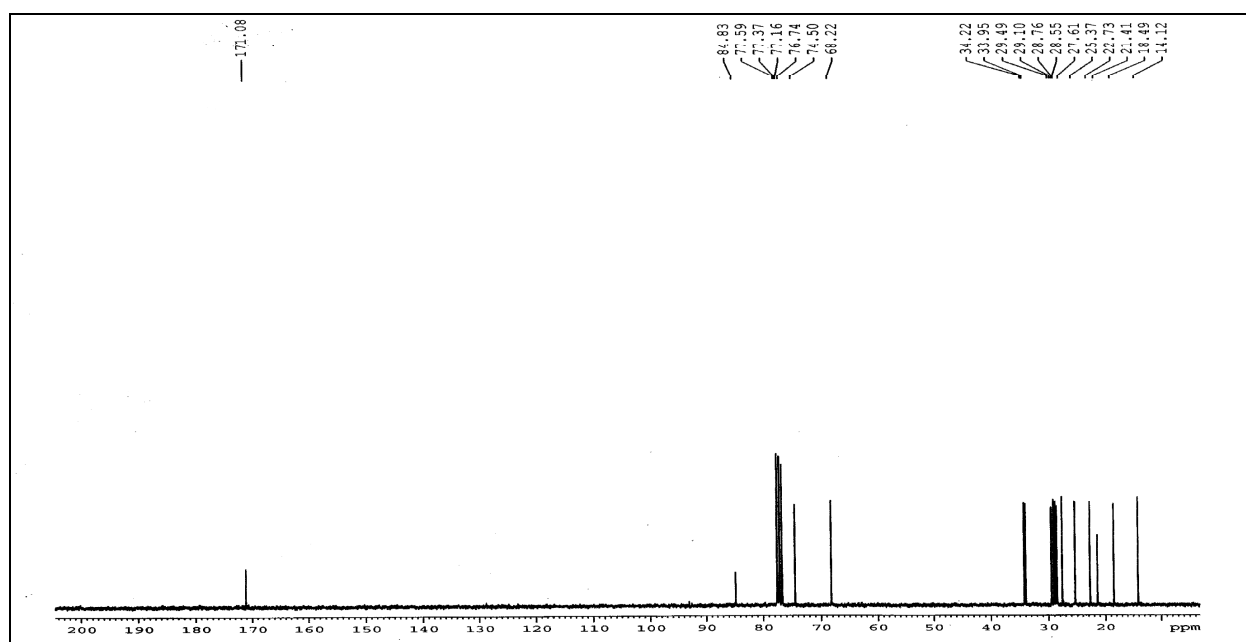
¹³C NMR spectrum of 20 (75 MHz, CDCl₃):



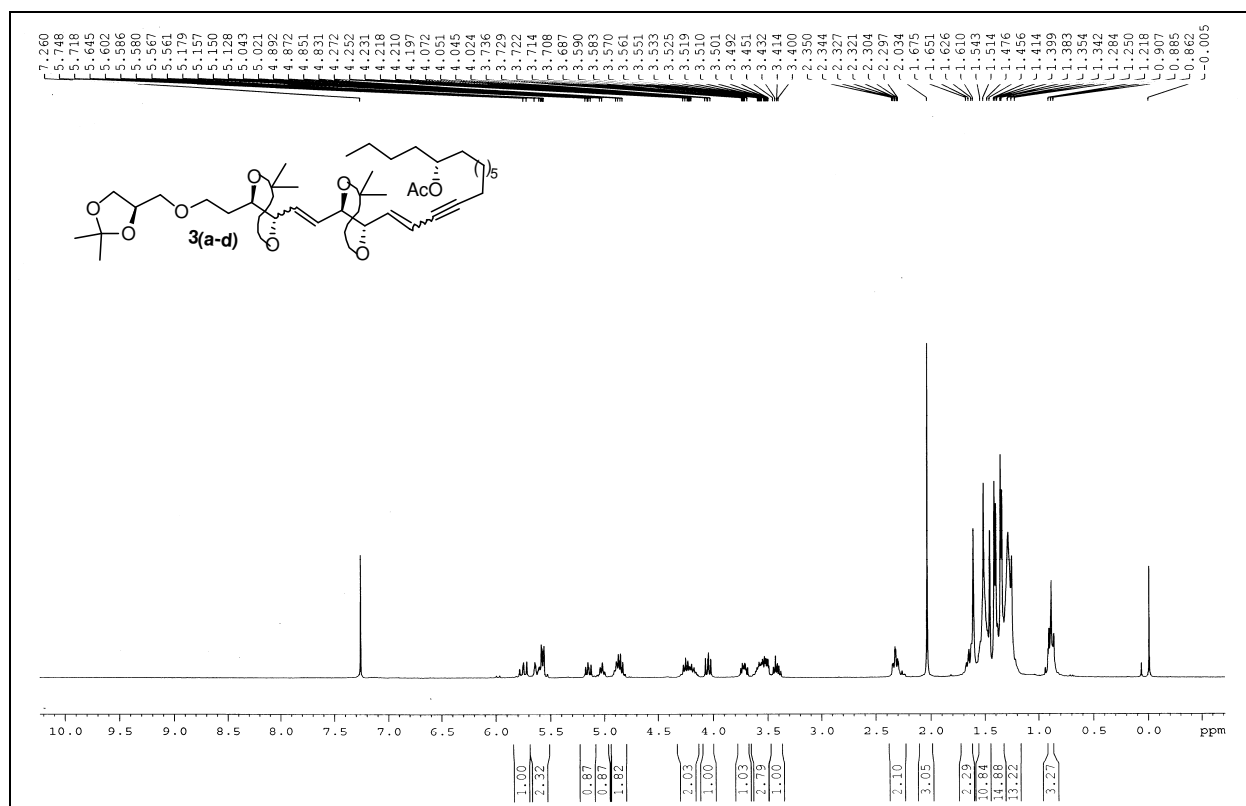
^1H NMR spectrum of 5 (500 MHz, CDCl_3):



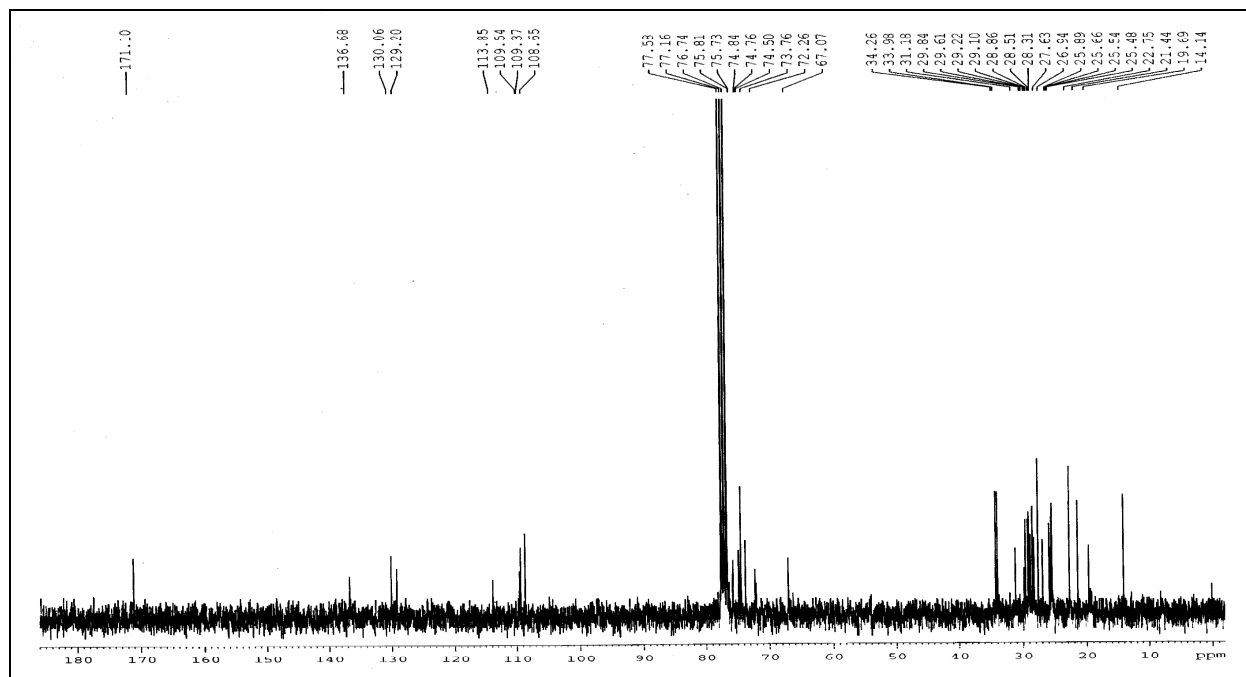
^{13}C NMR spectrum of 5 (75 MHz, CDCl_3):



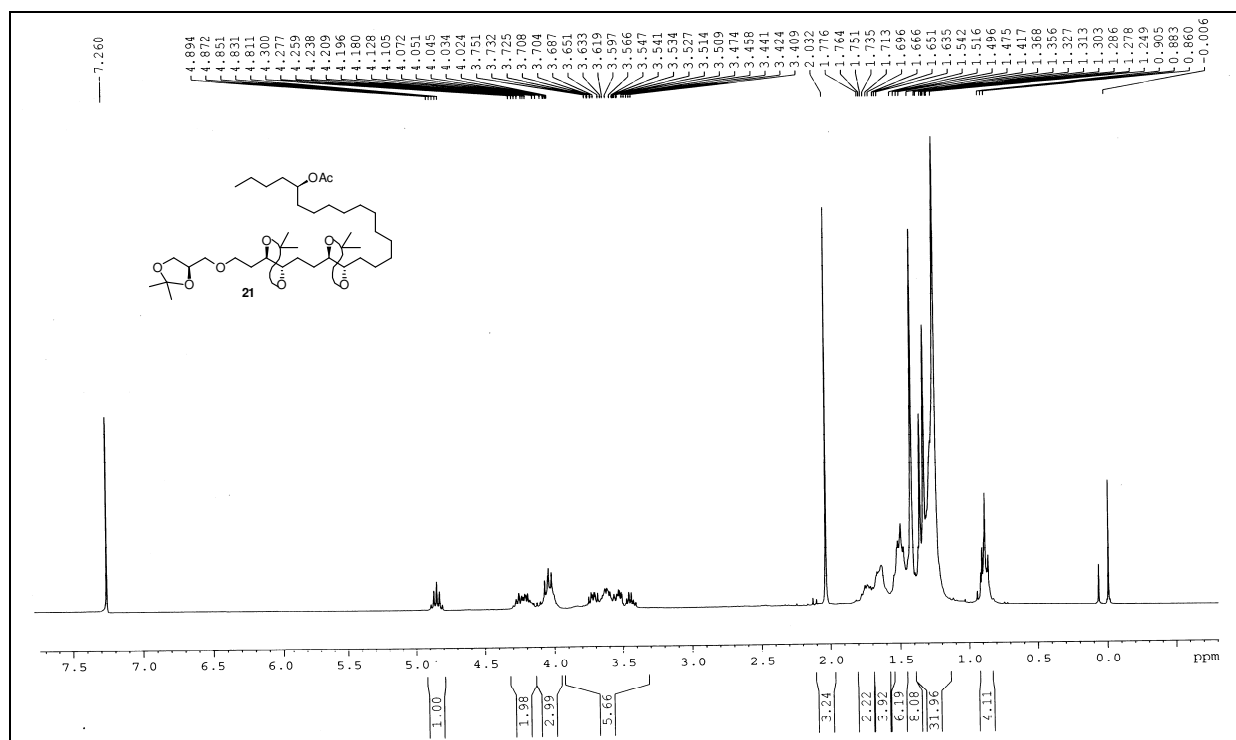
^1H NMR spectrum of diastereomeric mixture of 3(a-d) (300 MHz, CDCl_3):



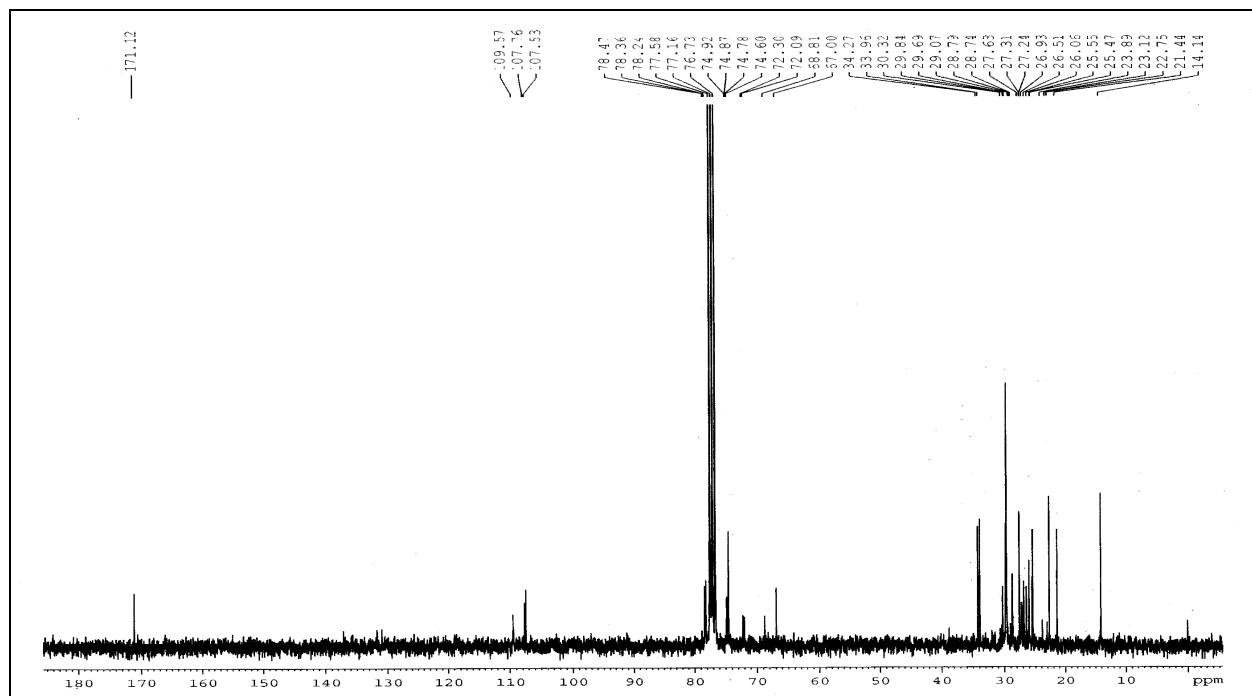
^{13}C NMR spectrum of diastereomeric mixture of 3(a-d) (75 MHz, CDCl_3):



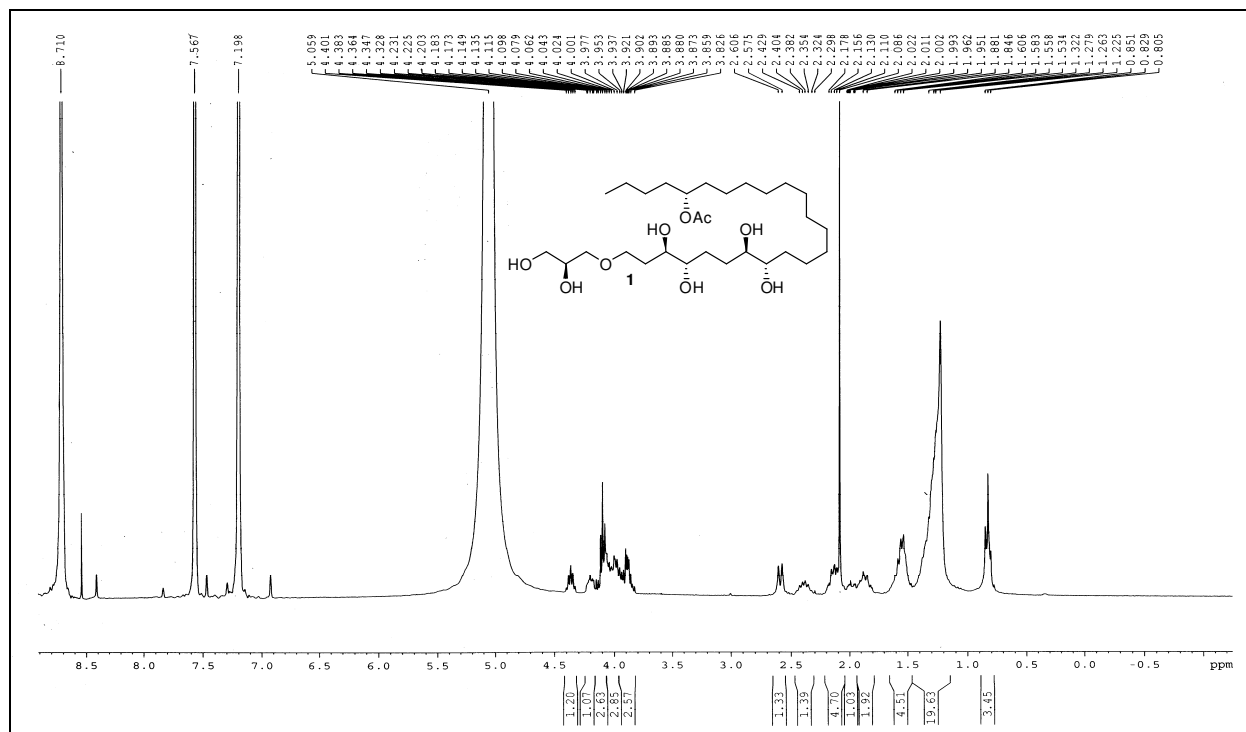
^1H NMR spectrum of 21 (300 MHz, CDCl_3):



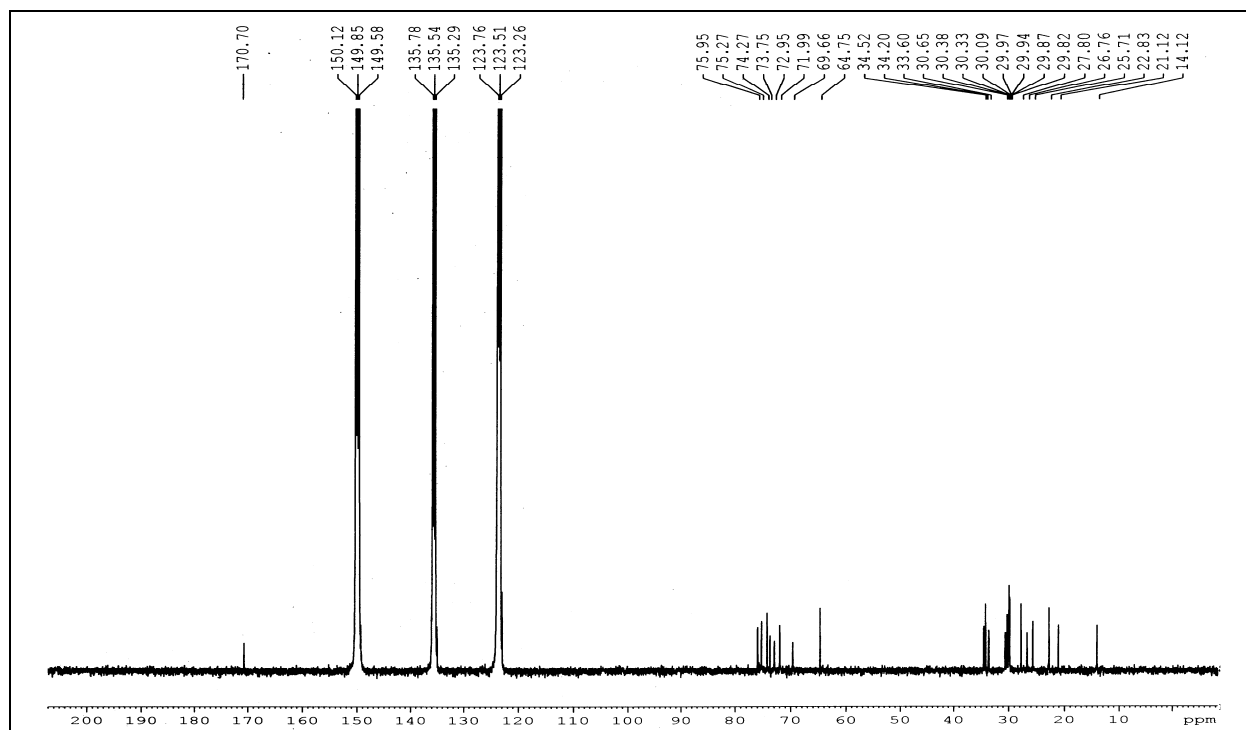
^{13}C NMR spectrum of 21 (75 MHz, CDCl_3):



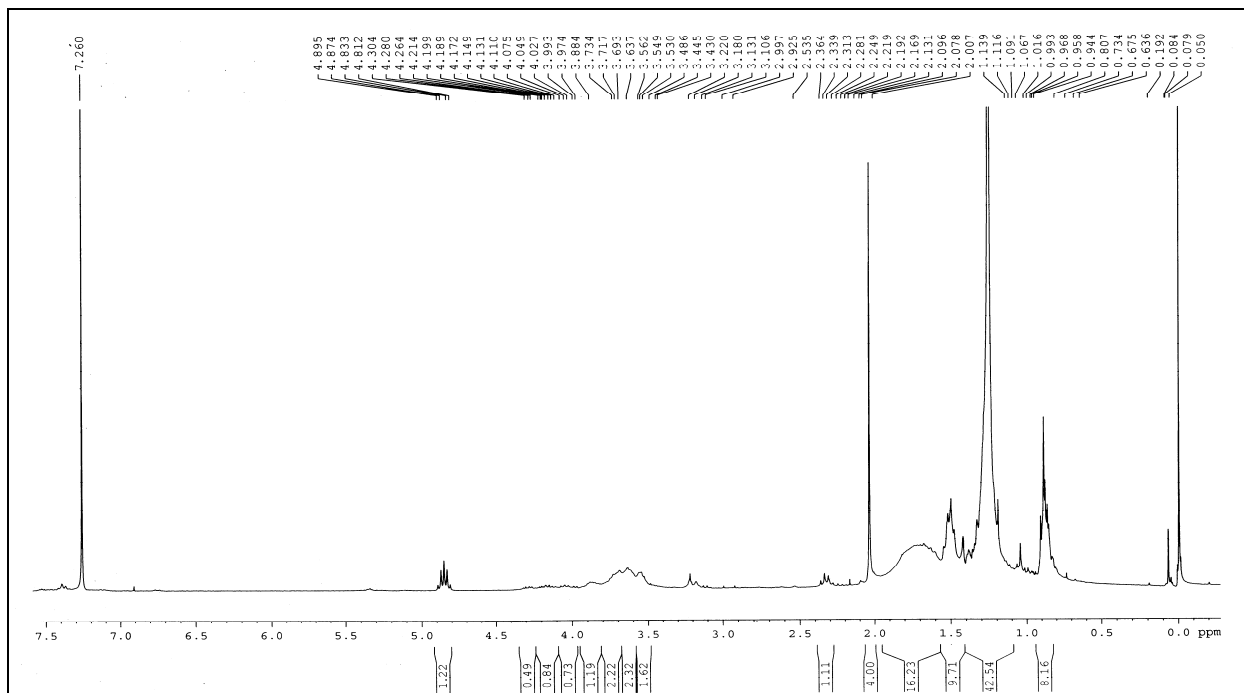
^1H NMR spectrum of 1 (300 MHz, $\text{C}_5\text{D}_5\text{N}$):



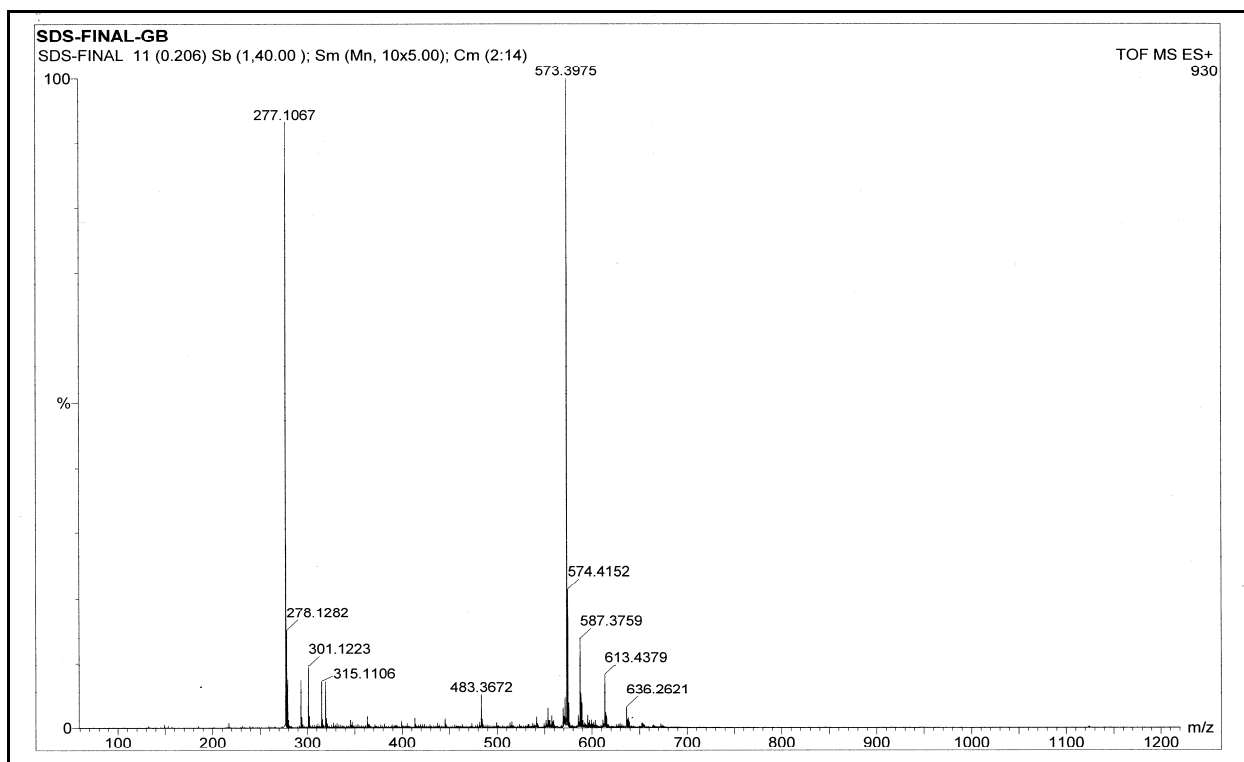
^{13}C NMR spectrum of 1 (100 MHz, $\text{C}_5\text{D}_5\text{N}$):



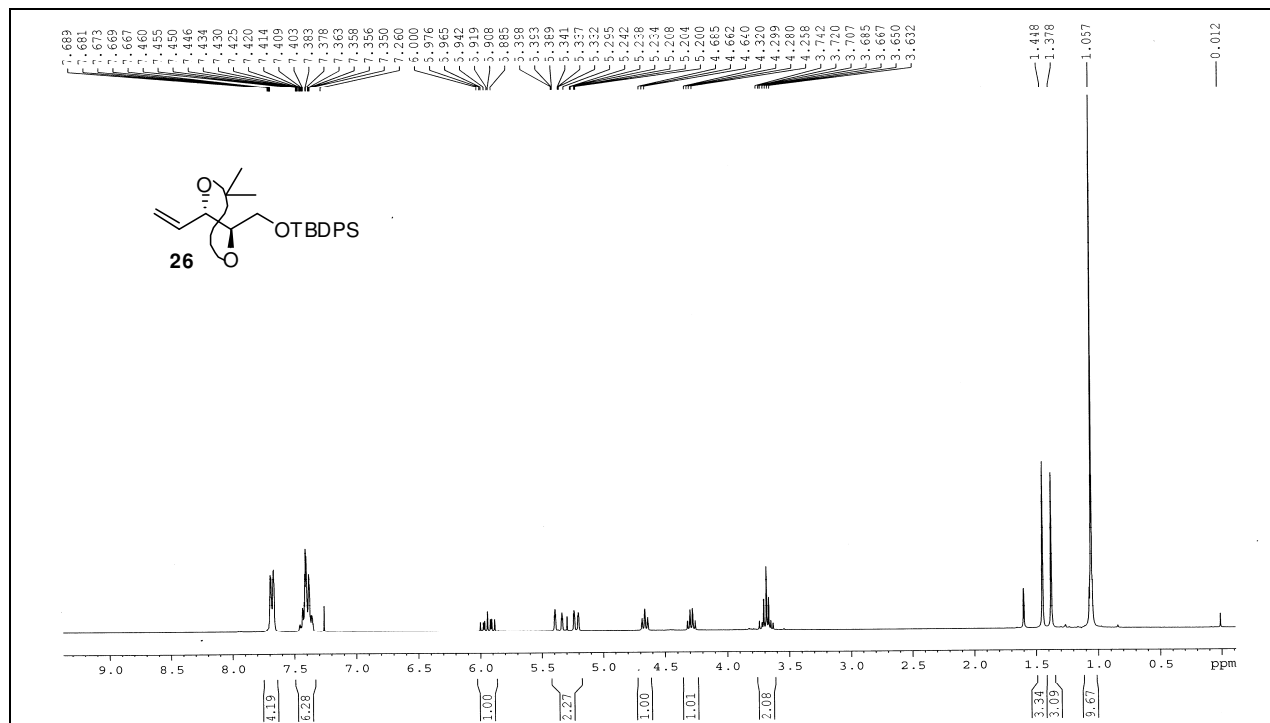
^1H NMR spectrum of 1 (300 MHz, CDCl_3):



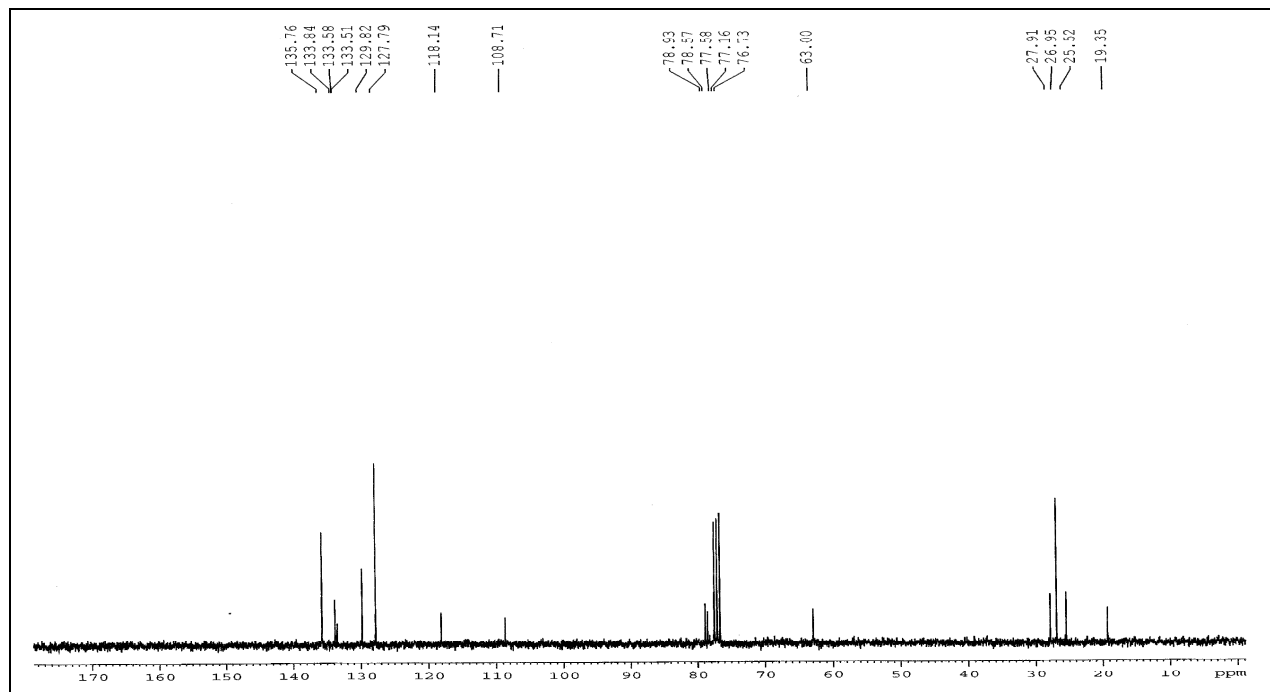
HRMS spectrum of 1:



^1H NMR spectrum of 26 (300 MHz, CDCl_3):



^{13}C NMR spectrum of 26 (75 MHz, CDCl_3):



Chemical structure of compound 27 is shown above the spectrum. The structure is a bicyclic molecule with a hydroxyl group (HO) and a tert-butyldimethylsilyl ether (OTBDPS) group.

The ^1H NMR spectrum (400 MHz, CDCl_3) displays the following chemical shifts (ppm): 1.065, 1.374, 1.331, 1.875, 1.903, 1.914, 1.926, 2.404, 3.642, 3.684, 3.694, 3.729, 3.756, 3.778, 3.792, 3.804, 3.814, 3.827, 3.840, 3.855, 4.211, 4.224, 4.237, 4.244, 4.257, 4.268, 4.316, 4.365, 4.390, 4.397, 4.411, 5.293, 7.364, 7.368, 7.373, 7.385, 7.395, 7.402, 7.413, 7.434, 7.442, 7.451, 7.456, 7.648, 7.652, 7.658, 7.663, 7.667, 7.671, 7.678.

The spectrum shows several peaks corresponding to the protons in the molecule. The integration values are provided below the baseline:

- 1.00
- 1.51
- 0.18
- 0.18
- 0.45
- 0.52
- 0.16
- 0.36
- 0.60
- 0.59
- 2.28

135.70
133.29
133.16
130.10
129.96
127.99
127.89
108.29
77.85
77.58
77.36
77.16
77.00
76.73
62.64
61.57
31.63
28.17
26.96
25.65
19.30

Chemical structure of compound 28 is shown above the spectrum. The spectrum displays peaks from 0.007 to 7.681 ppm. Integration values are provided below the baseline, and chemical shift values are listed above the peaks.

Chemical Shift (ppm)	Integration
7.681	4.24
7.662	4.24
7.448	6.36
7.444	6.36
7.440	6.36
7.431	6.36
7.425	6.36
7.417	6.36
7.413	6.36
7.408	6.36
7.402	6.36
7.395	6.36
7.382	6.36
7.377	6.36
7.367	6.36
7.362	6.36
7.356	6.36
7.261	1.00
5.939	0.99
5.930	1.00
5.909	1.00
5.896	1.00
5.883	1.00
5.869	1.00
5.299	0.99
5.295	1.00
5.256	1.00
5.252	1.00
5.186	0.99
5.164	1.00
5.160	1.00
5.158	1.00
4.372	0.93
4.362	1.01
4.357	1.01
4.348	2.09
4.338	1.34
4.332	3.17
4.323	3.17
4.218	3.17
4.204	3.17
4.195	3.17
3.975	3.17
3.960	3.17
3.769	3.17
3.762	3.17
3.744	3.17
3.736	3.17
3.718	3.17
3.674	3.17
3.661	3.17
3.648	3.17
3.635	3.17
3.628	3.17
3.617	3.17
3.610	3.17
3.603	3.17
3.587	3.17
3.567	3.17
3.544	3.17
2.015	1.06
2.005	1.06
1.998	1.06
1.989	1.06
1.980	1.06
1.971	1.06
1.854	6.88
1.841	6.88
1.830	6.88
1.817	6.88
1.807	6.88
1.794	6.88
1.770	10.01
1.370	10.01
1.332	10.01
1.056	10.01
0.007	10.01

135.76
135.73
135.11
129.85
127.84
116.81
108.01
77.89
77.47
77.15
76.84
74.50
72.01
67.61
62.90
29.84
28.31
27.17
27.01
25.75
19.35

ppm

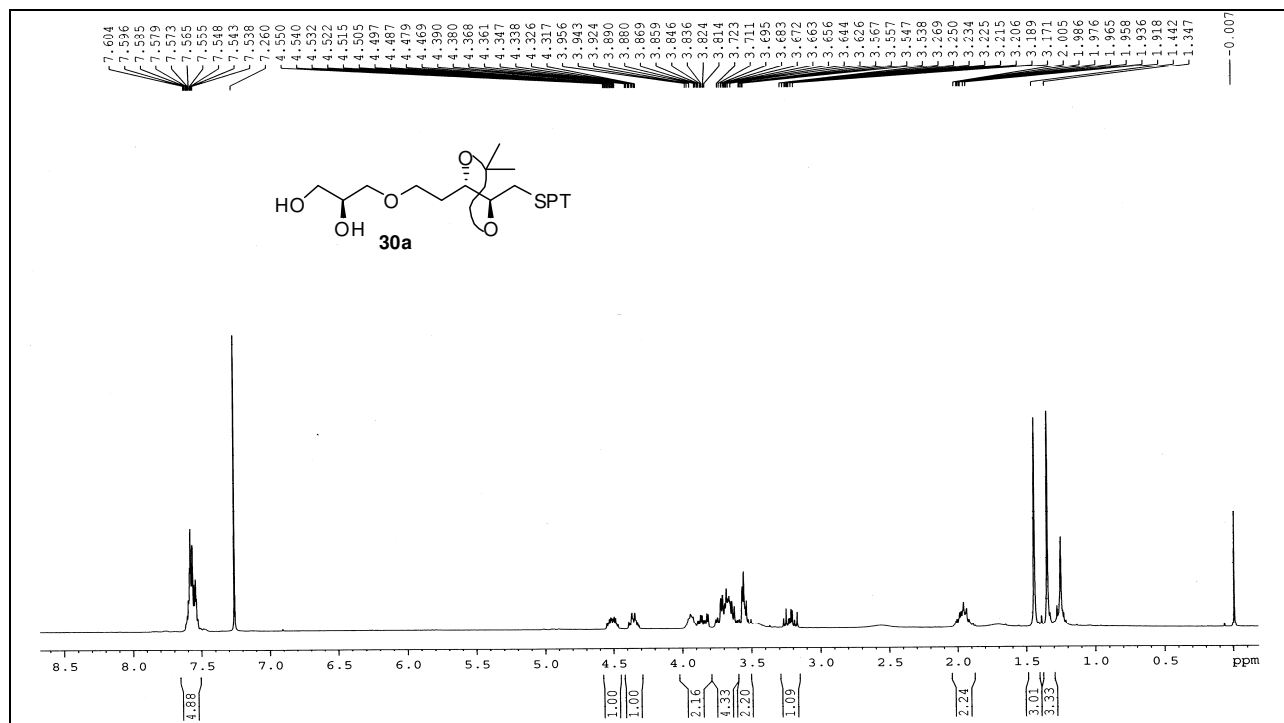
Chemical structure of compound 29 is shown above the spectrum. The structure is a bicyclic ether with a vinyl group and a side chain labeled SPT.

¹H NMR Spectrum (CDCl₃):

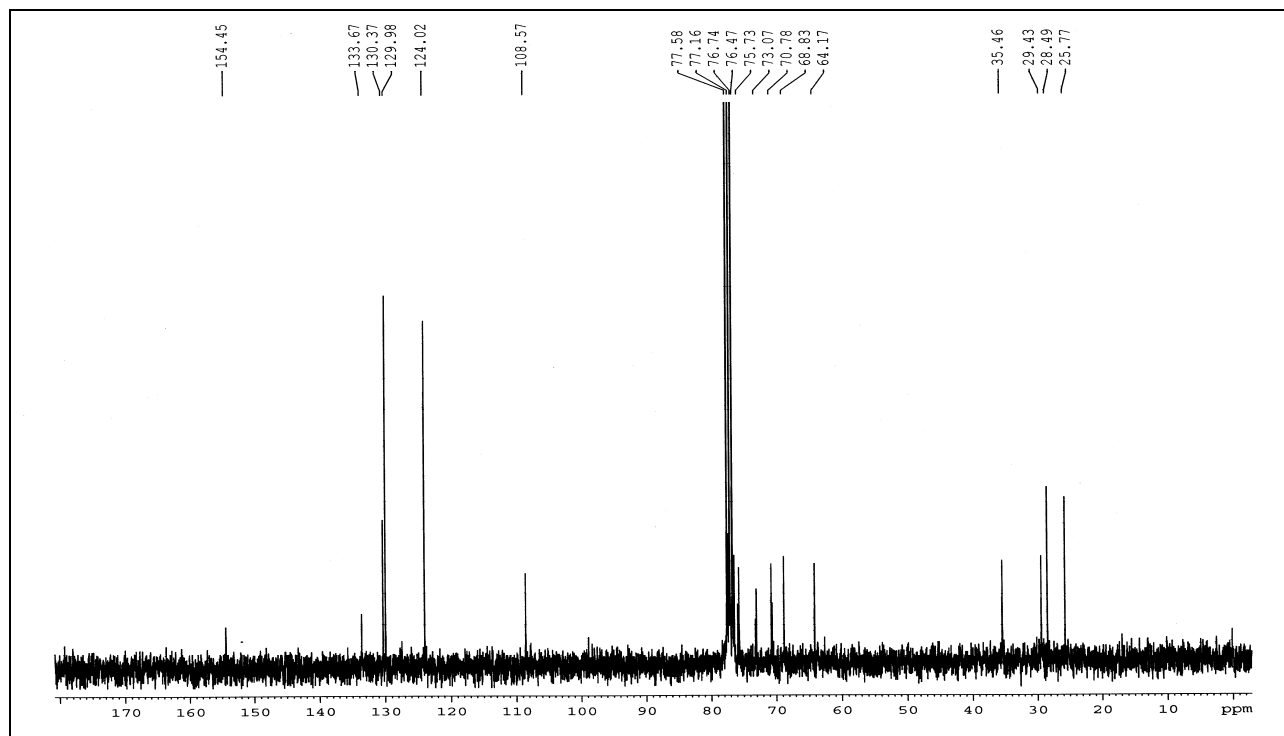
Chemical Shift (ppm)	Integration
7.539 - 7.530	1.73
6.0 - 6.1	1.06
5.0 - 5.2	1.90
4.5 - 4.6	1.92
4.0 - 4.1	1.87
3.5 - 3.6	2.93
3.0 - 3.1	1.06
2.0 - 2.1	2.18
1.5 - 1.6	2.78
1.4 - 1.5	2.92
0.0	-

154.45
134.84
130.27
129.96
123.98
117.17
108.80
77.53
77.16
76.74
75.95
75.27
72.22
67.10
35.29
29.89
28.47
25.80

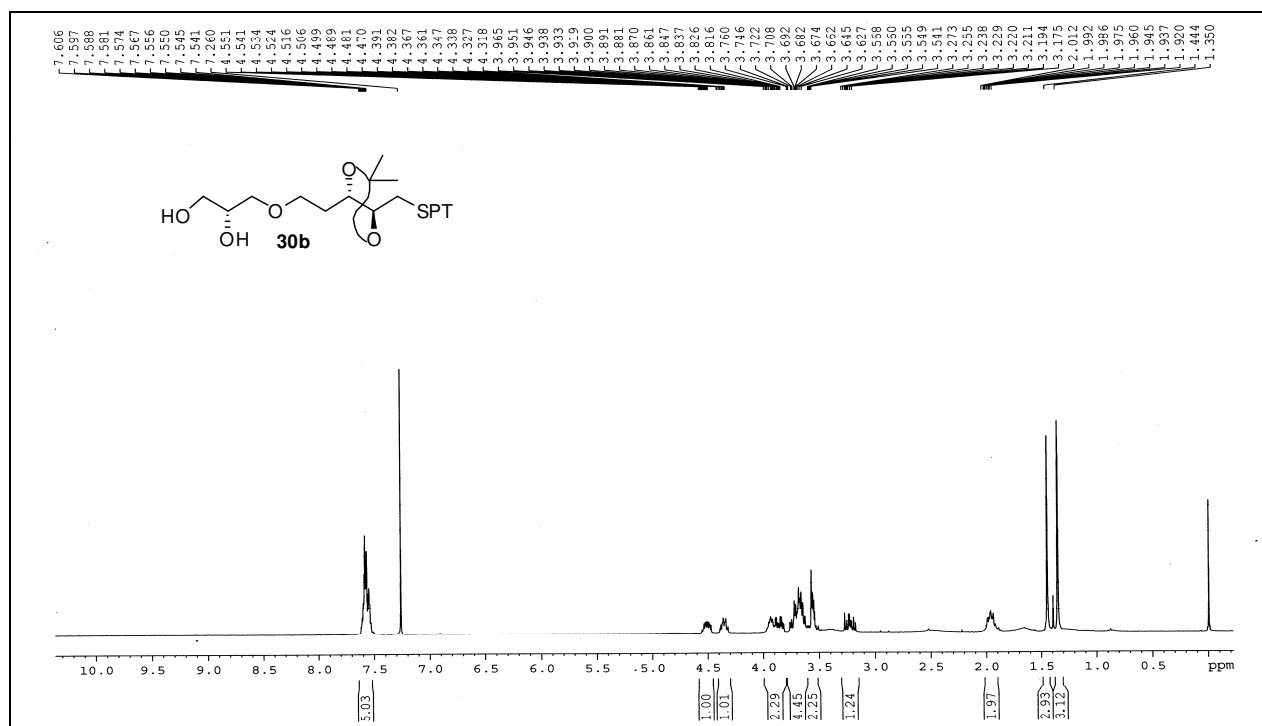
^1H NMR spectrum of 30a (300 MHz, CDCl_3):



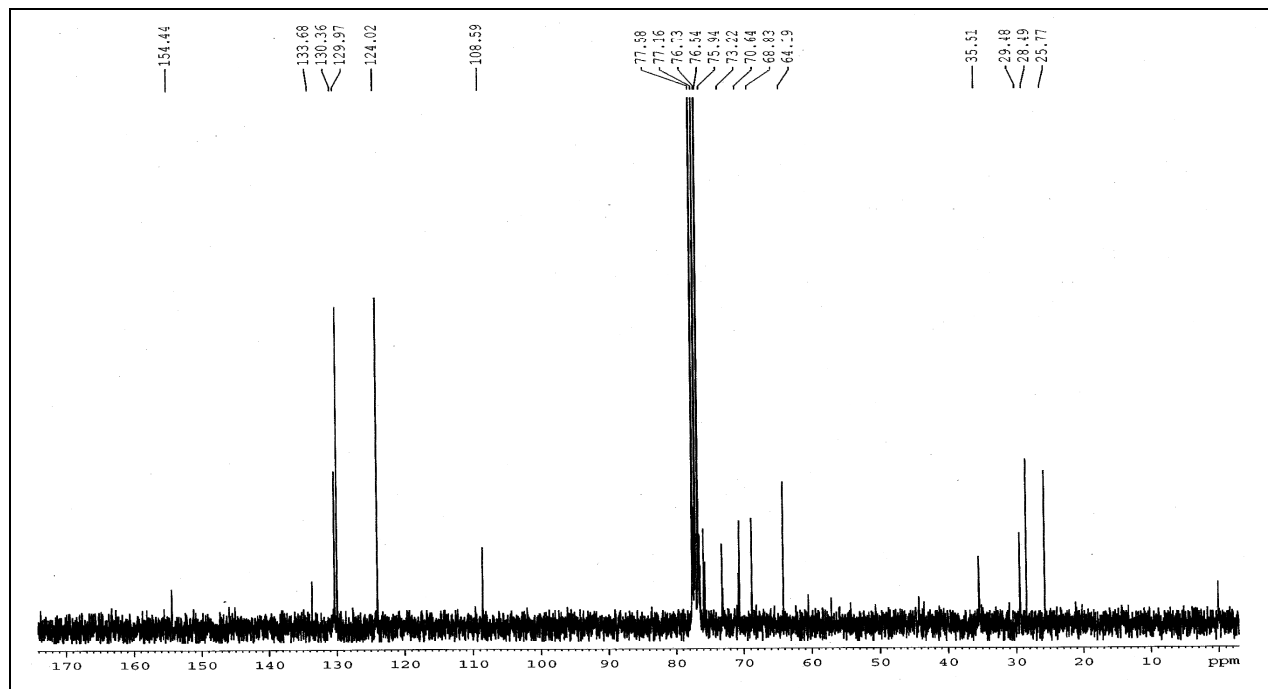
^{13}C NMR spectrum of 30a (75 MHz, CDCl_3):



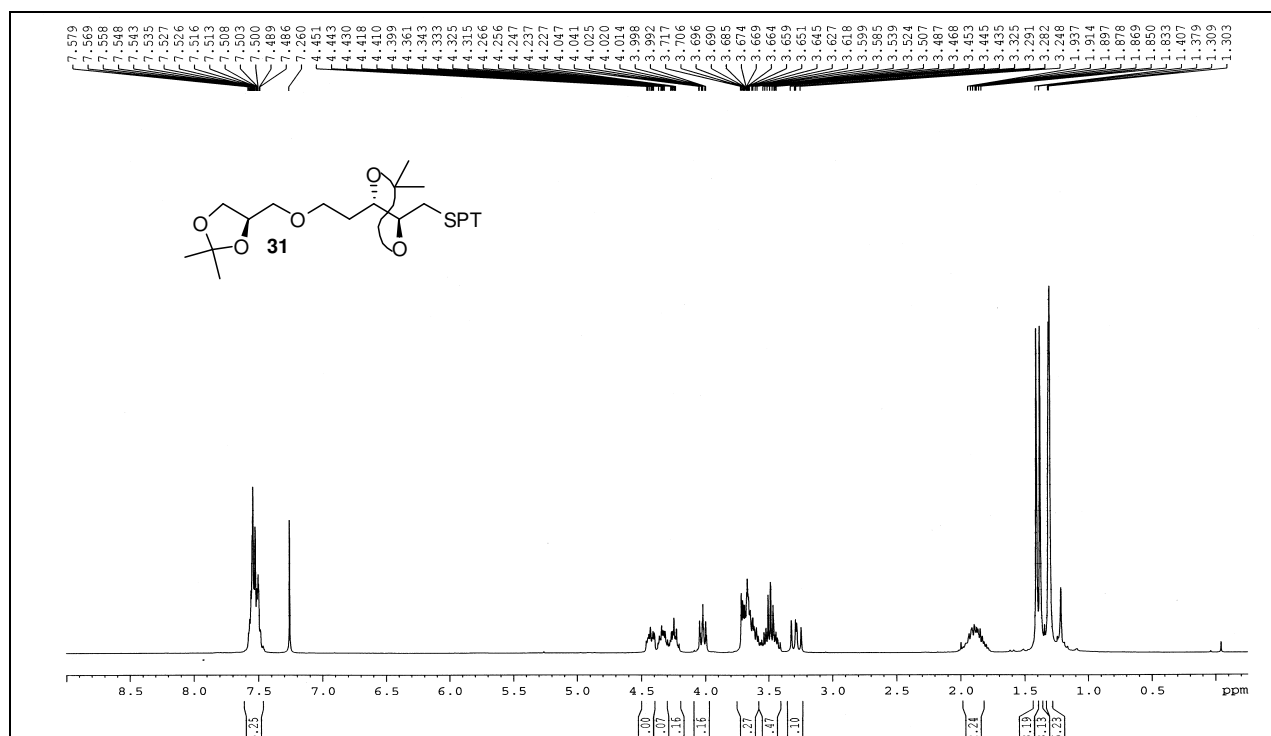
^1H NMR spectrum of 30b (300 MHz, CDCl_3):



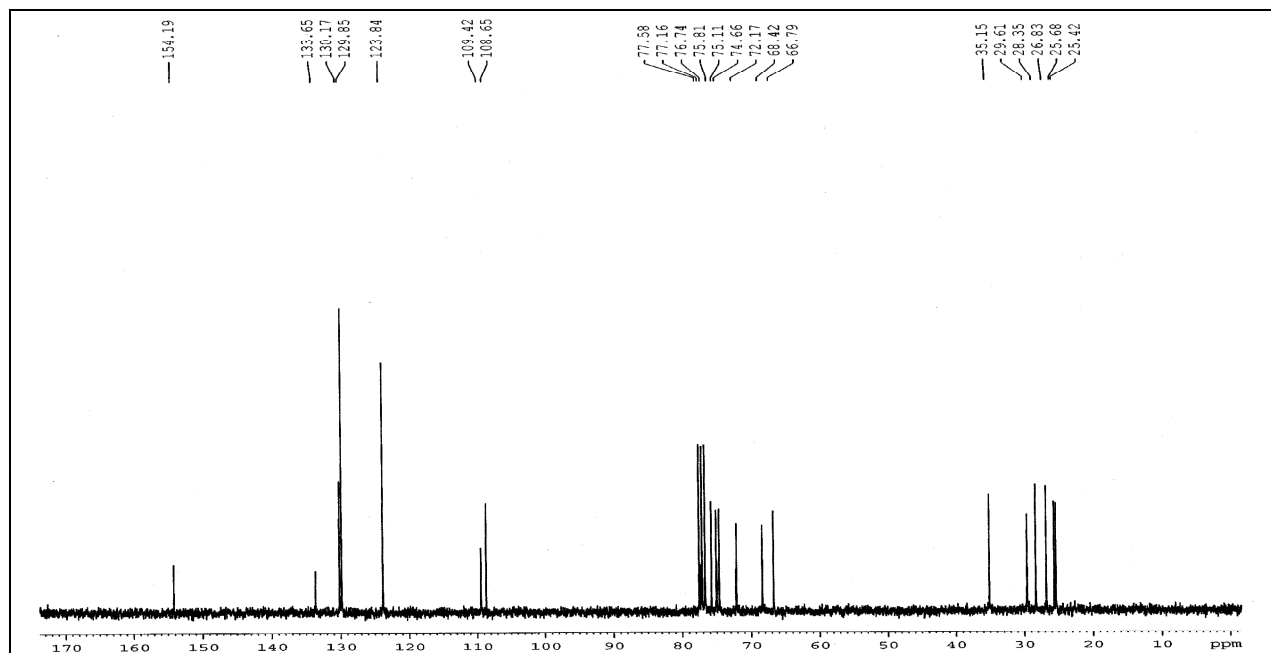
^{13}C NMR spectrum of 30b (75 MHz, CDCl_3):



^1H NMR spectrum of 31 (300 MHz, CDCl_3):



^{13}C NMR spectrum of 31 (75 MHz, CDCl_3):



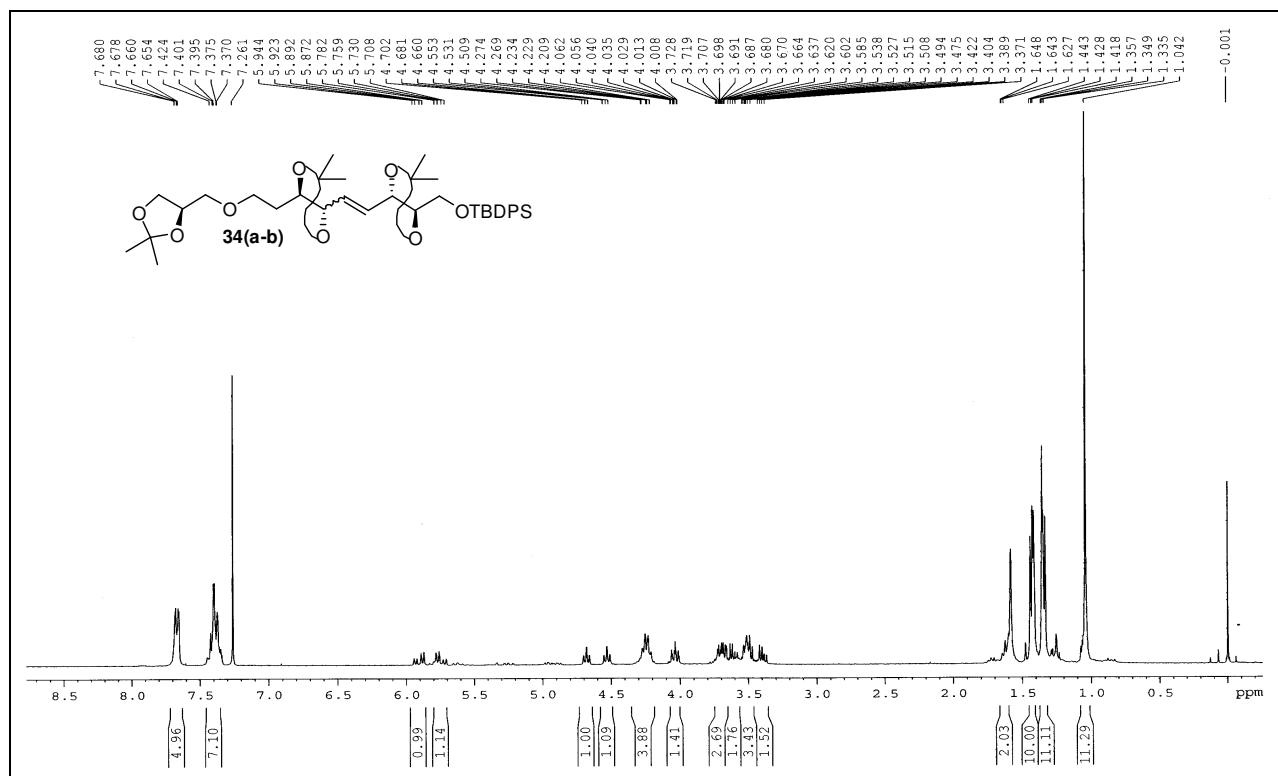
Chemical structure of compound 32 is shown above the spectrum. The structure is a complex molecule featuring a central carbon atom bonded to a tert-butyl group, a methoxy group, and a side chain containing an ether linkage and a sulfonate group (SO₂PT).

¹H NMR Spectrum (CDCl₃):

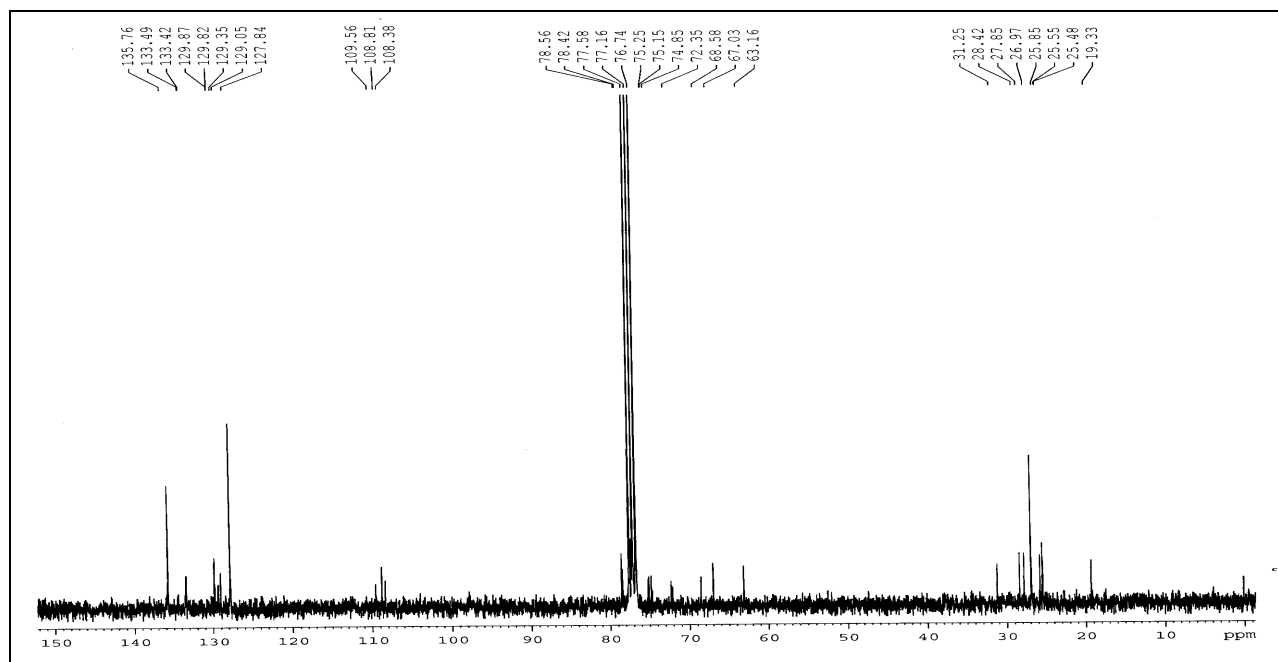
- Chemical Shifts (ppm):** 7.612, 7.601, 7.588, 7.569, 7.550, 7.520, 4.665, 4.644, 4.623, 4.602, 4.592, 4.574, 4.542, 4.320, 4.299, 4.277, 4.240, 4.232, 4.221, 4.212, 4.201, 4.193, 4.181, 4.162, 4.018, 3.996, 3.990, 3.981, 3.969, 3.959, 3.837, 3.817, 3.807, 3.681, 3.662, 3.653, 3.634, 3.618, 3.607, 3.586, 3.577, 3.551, 3.529, 3.505, 3.499, 3.486, 3.473, 3.453, 3.447, 3.434, 3.428, 3.417, 3.399, 1.827, 1.848, 1.811, 1.790, 1.372, 1.285, 1.237, 1.187, -0.024.
- Integrations:** 5.16, 5.16, 1.00, 1.04, 1.07, 1.09, 1.95, 2.07, 1.38, 1.96, 2.23, 3.34, 3.26, 4.09, 3.19.

154.16
133.35
131.40
129.39
125.93
109.51
109.30
77.59
77.16
76.74
75.68
74.49
72.58
72.45
68.46
66.70
56.45
29.48
27.42
26.86
25.62
25.29

^1H NMR spectrum of 34(a-b) (300 MHz, CDCl_3):



^{13}C NMR spectrum of 34(a-b) (75 MHz, CDCl_3):



Chemical structure of **35(a-d)** is shown above the spectrum. The structure is a complex molecule with two quaternary carbons, each bonded to two methyl groups and a hydrogen atom. It features a central double bond, a terminal vinyl group, and a terminal alkyne group. The molecule is substituted with a 2,2,6,6-tetramethyl-1,3-dioxane-5-yl group and a 2,2,6,6-tetramethyl-1,3-dioxane-5-yl group.

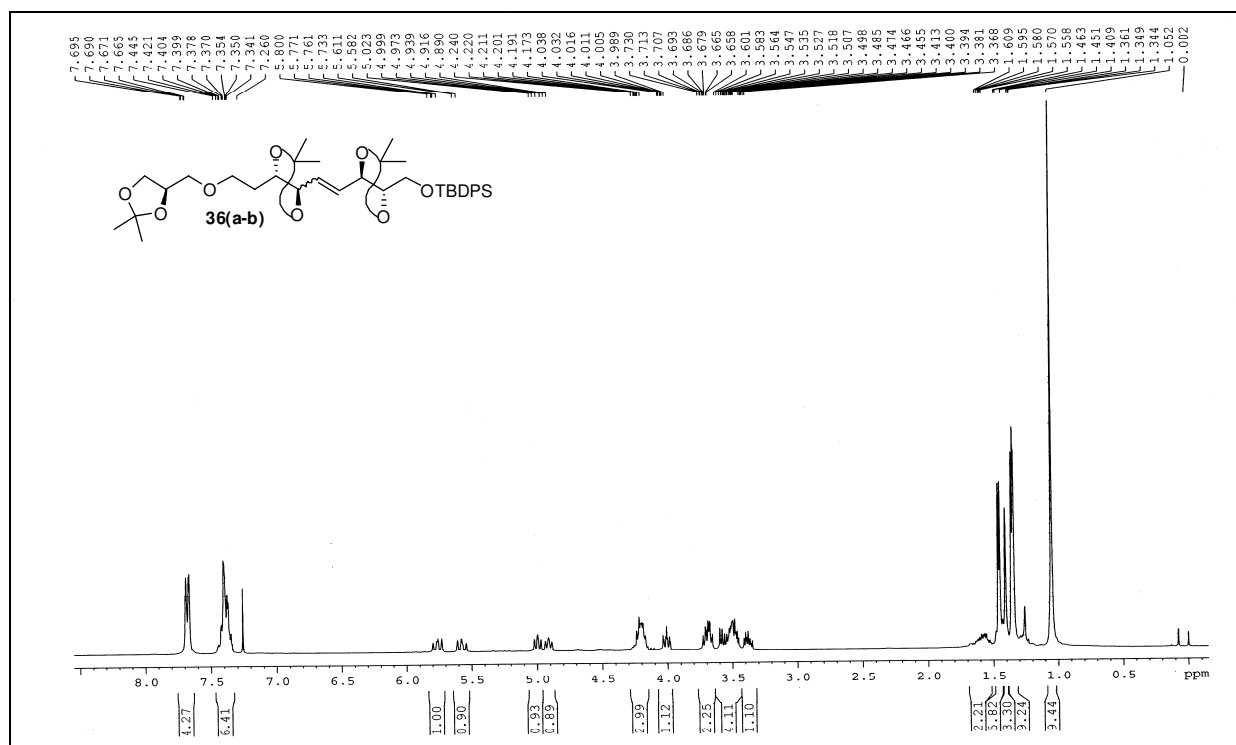
¹H NMR spectrum (CDCl₃) of compound **35(a-d)**. The x-axis represents the chemical shift in ppm, ranging from 0 to 7. The spectrum shows several peaks, with integration values provided below the baseline. The chemical structure of **35(a-d)** is shown above the spectrum.

Chemical Shift (ppm)	Integration
7.260	
6.475	
6.471	
6.449	
6.445	
6.317	
6.292	
6.266	
5.746	
5.718	
5.694	
5.637	
5.616	
5.582	
5.580	
4.895	
4.893	
4.876	
4.873	
4.852	
4.848	
4.795	
4.773	
4.752	
4.543	
4.521	
4.508	
4.482	
4.480	
4.276	
4.271	
4.258	
4.237	
4.073	
4.051	
4.045	
4.024	
3.747	
3.731	
3.726	
3.710	
3.704	
3.699	
3.683	
3.628	
3.609	
3.598	
3.588	
3.579	
3.561	
3.548	
3.539	
3.529	
3.516	
3.511	
3.497	
3.493	
3.473	
3.465	
3.451	
3.433	
3.418	
3.403	
3.393	
1.683	
1.507	
1.461	
1.417	
1.404	
1.379	
1.365	
1.356	
1.344	
-0.006	

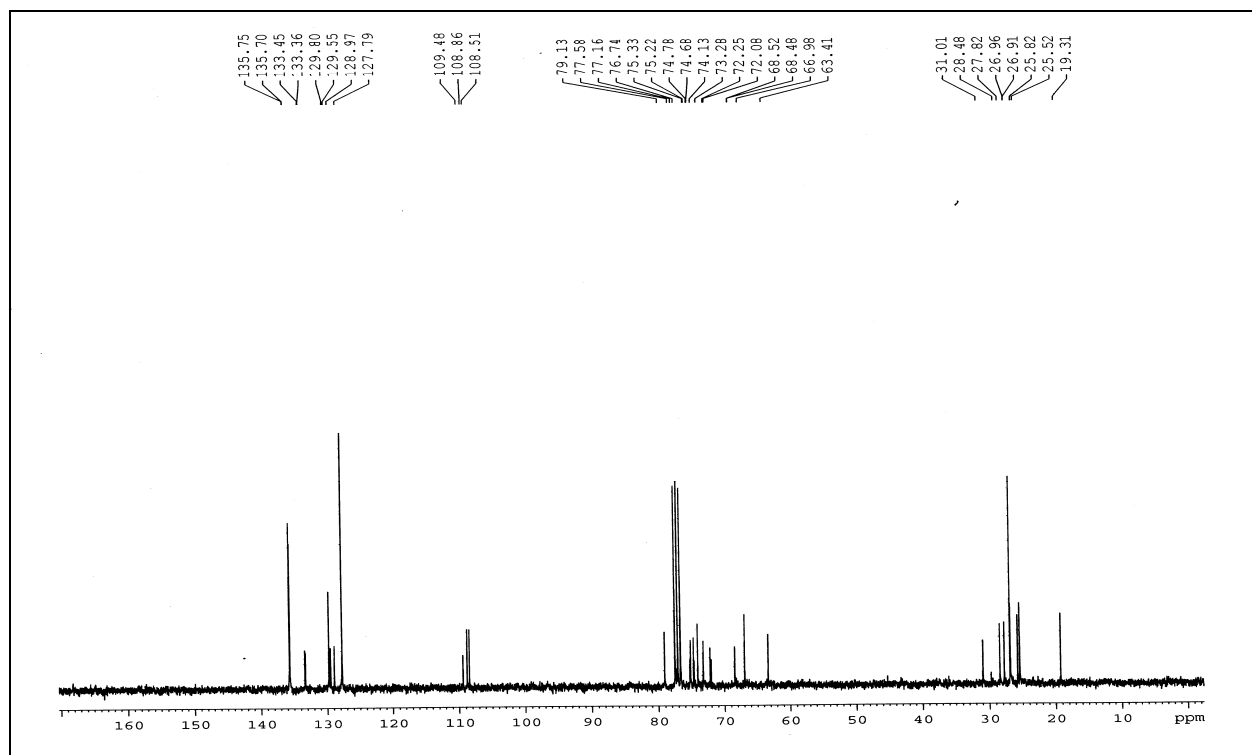
13C NMR spectrum (CDCl₃) of compound 10. The x-axis represents chemical shift in ppm, ranging from 160 to 20. The spectrum shows a large solvent peak at 77.16 ppm. Other labeled peaks include:

- 138.08
- 130.08
- 129.03
- 109.60
- 108.53
- 84.99
- 81.24
- 78.54
- 77.95
- 77.59
- 77.16
- 76.74
- 75.20
- 74.87
- 72.29
- 68.65
- 66.95
- 31.09
- 28.38
- 28.03
- 26.95
- 25.81
- 25.58
- 25.55

¹H NMR spectrum of 36(a-b) (300 MHz, CDCl₃):



^{13}C NMR spectrum of 36(a-b) (75 MHz, CDCl_3):



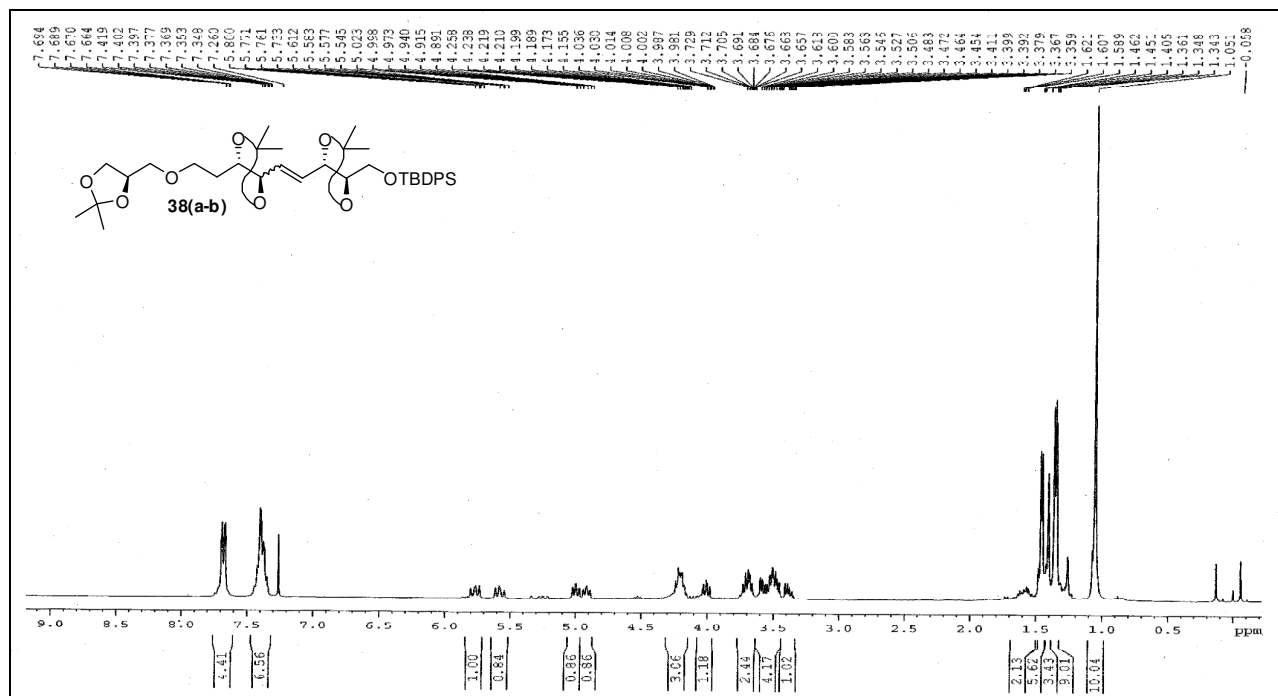
Chemical structure of 37(a-d) is shown above the spectrum. The structure is a complex molecule featuring a central carbon-carbon double bond, two quaternary carbon atoms, and two acetal protecting groups. The acetal groups are formed from a 1,3-diol and a ketone, with the ketone oxygen being part of a five-membered ring. The molecule is labeled 37(a-d).

¹H NMR spectrum (CDCl₃) of compound 37(a-d). The x-axis represents the chemical shift in ppm, ranging from 0.003 to 7.260. The spectrum shows several peaks, with integration values provided below the baseline. The peaks are assigned to the following protons in the molecule:

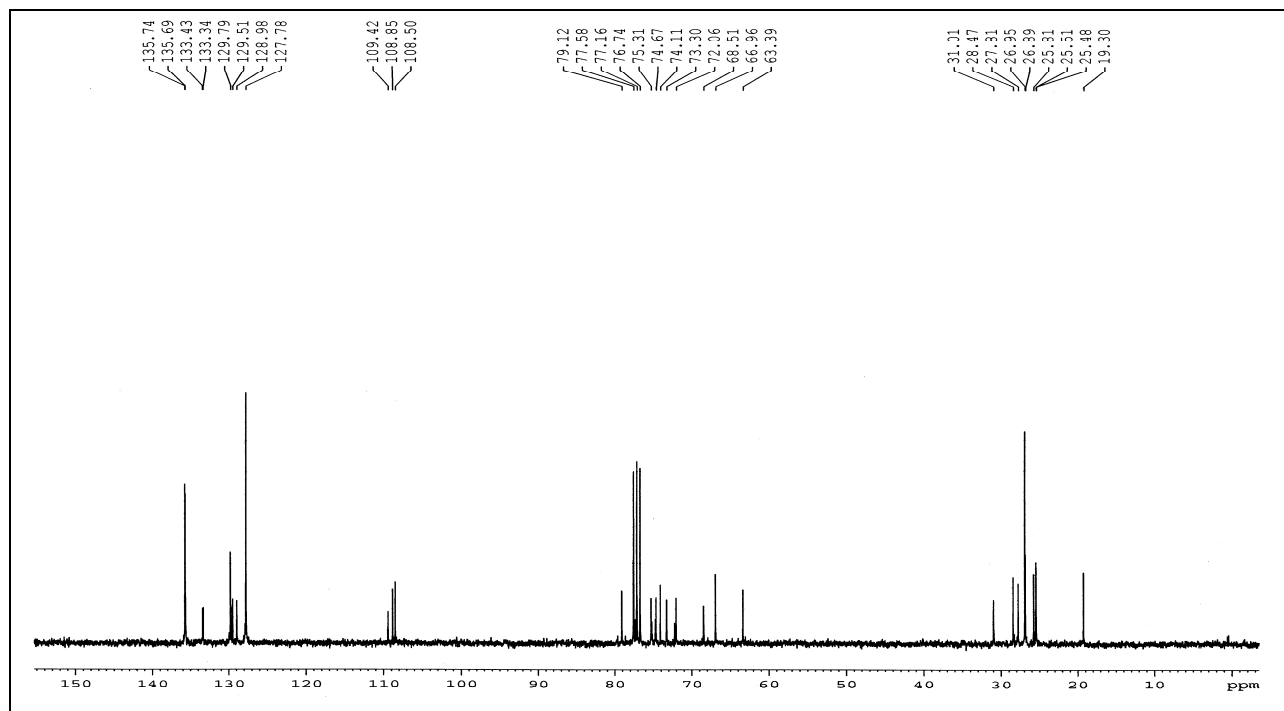
- 7.260 ppm (s, 1H, integration 0.38)
- 6.500 ppm (s, 1H, integration 1.00)
- 5.800 ppm (s, 1H, integration 1.37)
- 5.500 ppm (s, 1H, integration 1.95)
- 4.800 ppm (s, 1H, integration 3.71)
- 4.500 ppm (s, 1H, integration 1.59)
- 4.200 ppm (s, 1H, integration 2.27)
- 3.800 ppm (s, 1H, integration 4.37)
- 3.500 ppm (s, 1H, integration 1.51)
- 3.200 ppm (s, 1H, integration 1.00)
- 3.000 ppm (s, 1H, integration 1.00)
- 2.800 ppm (s, 1H, integration 1.00)
- 2.600 ppm (s, 1H, integration 1.00)
- 2.400 ppm (s, 1H, integration 1.00)
- 2.200 ppm (s, 1H, integration 1.00)
- 2.000 ppm (s, 1H, integration 1.00)
- 1.800 ppm (s, 1H, integration 1.00)
- 1.600 ppm (s, 1H, integration 1.00)
- 1.400 ppm (s, 1H, integration 1.00)
- 1.200 ppm (s, 1H, integration 1.00)
- 1.000 ppm (s, 1H, integration 1.00)
- 0.800 ppm (s, 1H, integration 1.00)
- 0.600 ppm (s, 1H, integration 1.00)
- 0.400 ppm (s, 1H, integration 1.00)
- 0.200 ppm (s, 1H, integration 1.00)
- 0.003 ppm (s, 1H, integration 1.00)

138.11
130.10
129.04
109.84
109.60
108.54
84.28
81.66
78.56
78.61
77.59
77.16
76.44
75.22
74.89
74.78
72.31
68.69
67.94
66.97
31.11
29.94
28.48
28.39
28.74
26.56
25.32
25.57

¹H NMR spectrum of 38(a-b) (300 MHz, CDCl₃):



^{13}C NMR spectrum of 38(a-b) (75 MHz, CDCl_3):



Chemical structure of **39(a-d)** is shown above the spectrum. The structure is a complex molecule featuring a central carbon-carbon double bond, multiple oxygen-containing functional groups (including a cyclic acetal and a cyclic ether), and a terminal vinyl group.

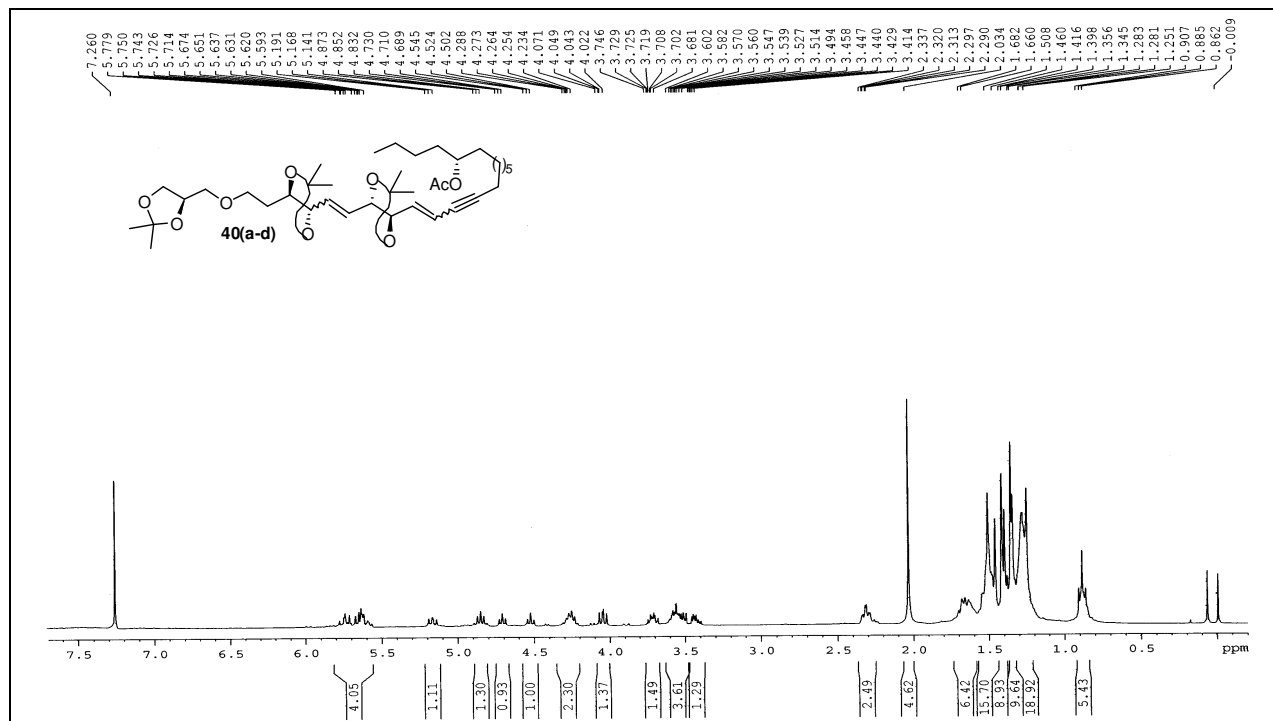
The ¹H NMR spectrum (CDCl₃) displays the following chemical shifts (ppm) and integrations:

Chemical Shift (ppm)	Integration
7.263	
6.508	
6.499	
6.497	
6.484	
6.482	
5.473	
5.297	
5.291	
5.271	
5.04	
5.045	
5.038	
5.037	
5.034	
5.020	
4.941	
4.917	
4.944	
4.855	
4.856	
4.851	
4.848	
4.800	
4.770	
4.743	
4.742	
4.741	
4.718	
4.747	
4.714	
4.632	
4.647	
4.625	
3.753	
3.732	
3.727	
3.705	
3.681	
3.683	
3.593	
3.583	
3.571	
3.561	
3.551	
3.533	
3.519	
3.500	
3.463	
3.445	
3.430	
3.412	
1.678	
1.656	
1.633	
1.611	
1.512	
1.460	
1.417	
1.408	
1.356	

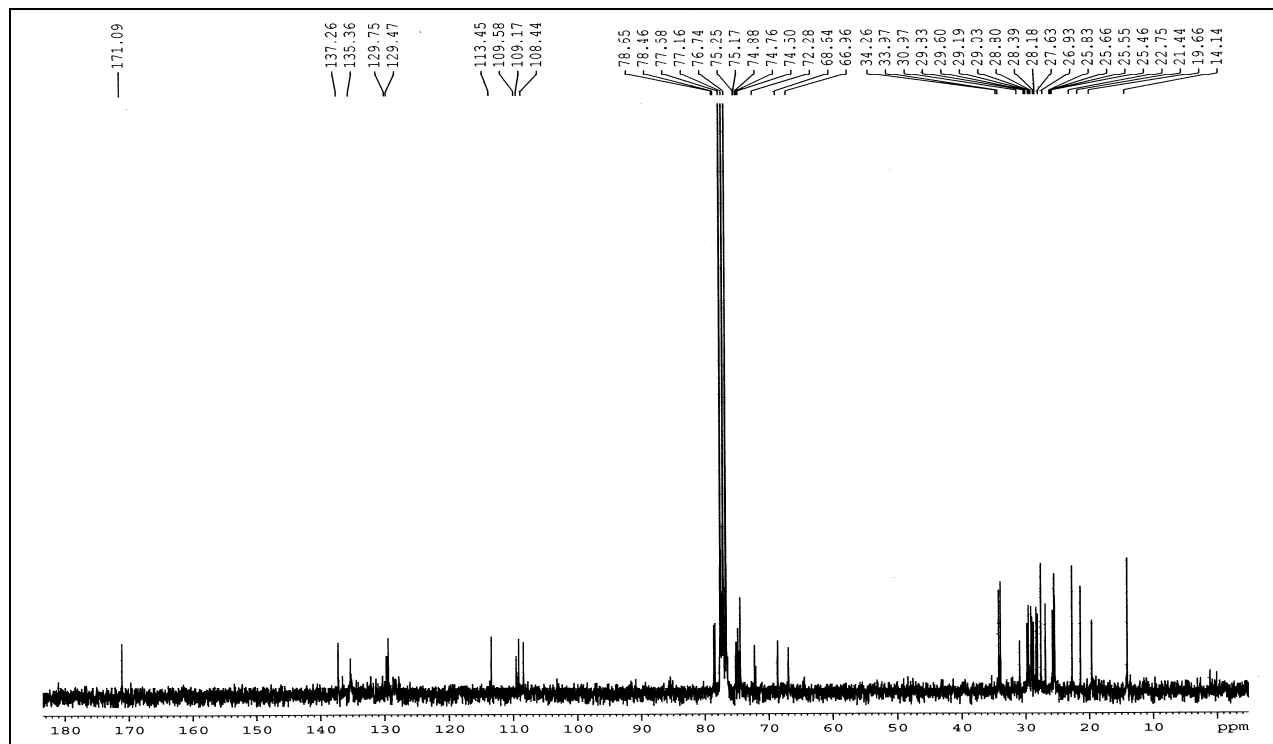
Chemical shift values (ppm) labeled on the spectrum:

- 137.365
- 129.916
- 129.083
- 109.804
- 109.517
- 108.755
- 85.711
- 81.414
- 77.586
- 77.163
- 76.739
- 75.665
- 74.896
- 74.760
- 73.924
- 73.755
- 72.137
- 58.821
- 57.027
- 31.321
- 29.834
- 28.481
- 28.203
- 26.964
- 25.874
- 25.689
- 25.557

^1H NMR spectrum of 40 (a-d) (300 MHz, CDCl_3):



^{13}C NMR spectrum of 40 (a-d) (75 MHz, CDCl_3):



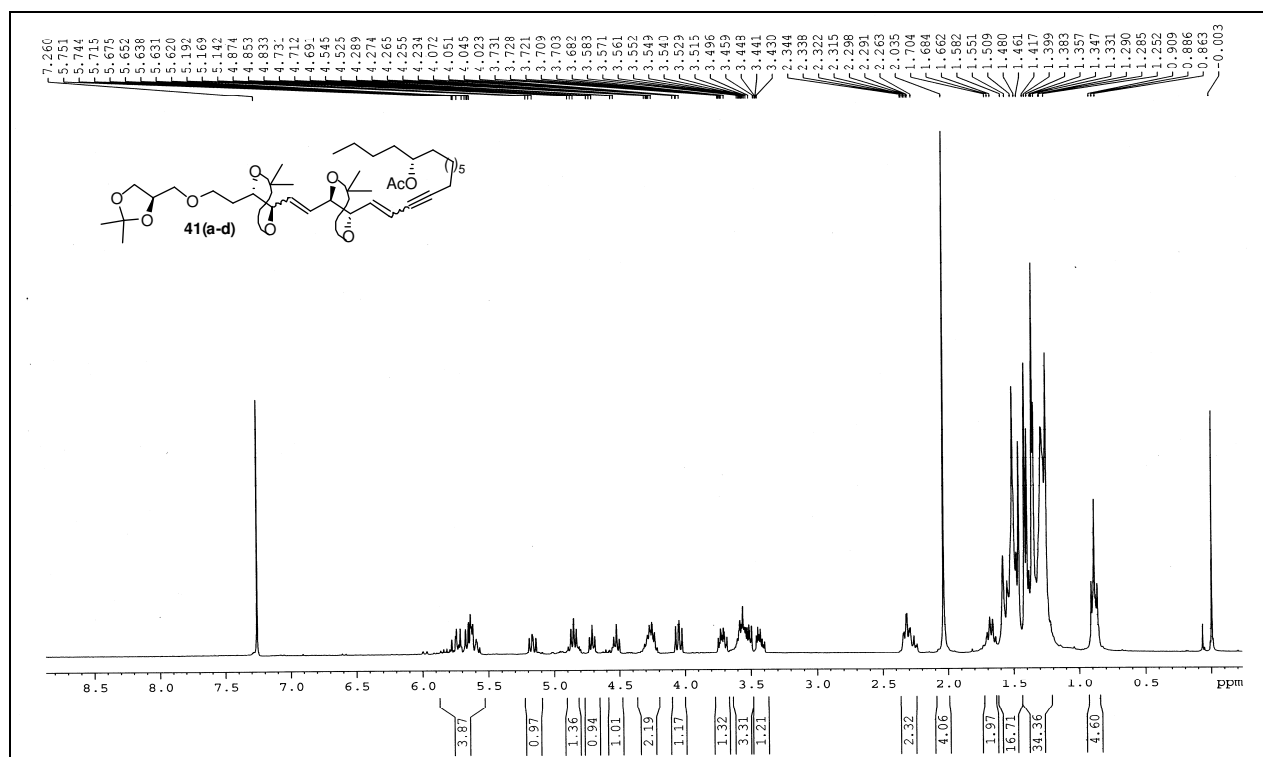
Chemical structure **22** is shown above the ¹H NMR spectrum. The structure is a complex molecule featuring a central carbon atom bonded to a tert-butyl group, a 2,2,4,4-tetramethyl-1,3-dioxane-5-yl group, a 2,2,4,4-tetramethyl-1,3-dioxane-5-yl group, and a 2,2,4,4-tetramethyl-1,3-dioxane-5-yl group. The molecule also contains a long alkyl chain and an acetate group (OAc).

The ¹H NMR spectrum (CDCl₃) displays the following chemical shifts (ppm) and integrations:

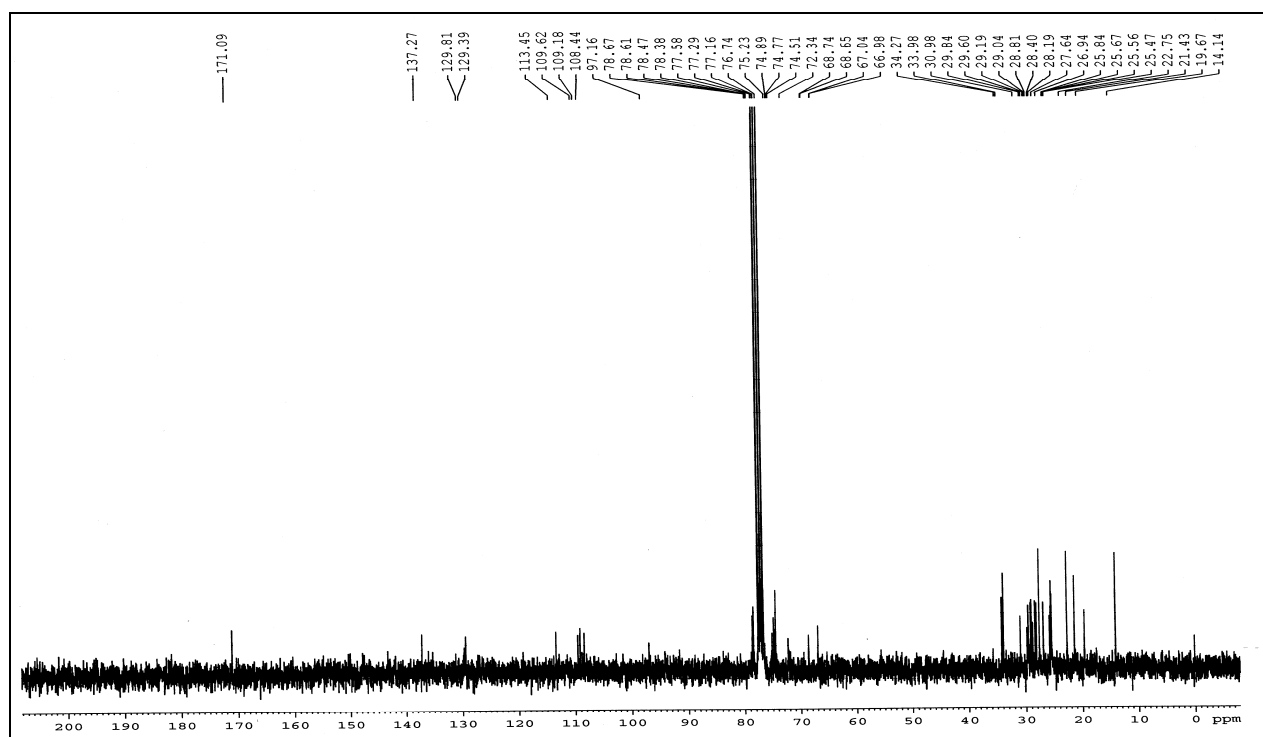
- 7.260 (1.01)
- 4.894, 4.874, 4.853, 4.832, 4.811, 4.284, 4.264, 4.244, 4.221, 4.201, 4.178, 4.111, 4.074, 4.052, 4.047, 4.026, 3.752, 3.734, 3.713, 3.707, 3.686, 3.653, 3.632, 3.632, 3.620, 3.598, 3.584, 3.569, 3.549, 3.536, 3.529, 3.516, 3.510, 3.480, 3.462, 3.440, 3.430, 3.413, 2.034, 1.782, 1.761, 1.739, 1.716, 1.517, 1.497, 1.480, 1.419, 1.336, 1.268, 1.280, 1.251, 0.906, 0.884, 0.861, -0.008

The spectrum shows a complex pattern of peaks, including a sharp singlet at 7.260 ppm, a broad multiplet between 4.0 and 5.0 ppm, a sharp singlet at 2.034 ppm, and a broad multiplet between 1.0 and 2.0 ppm. The integration values are provided below the baseline.

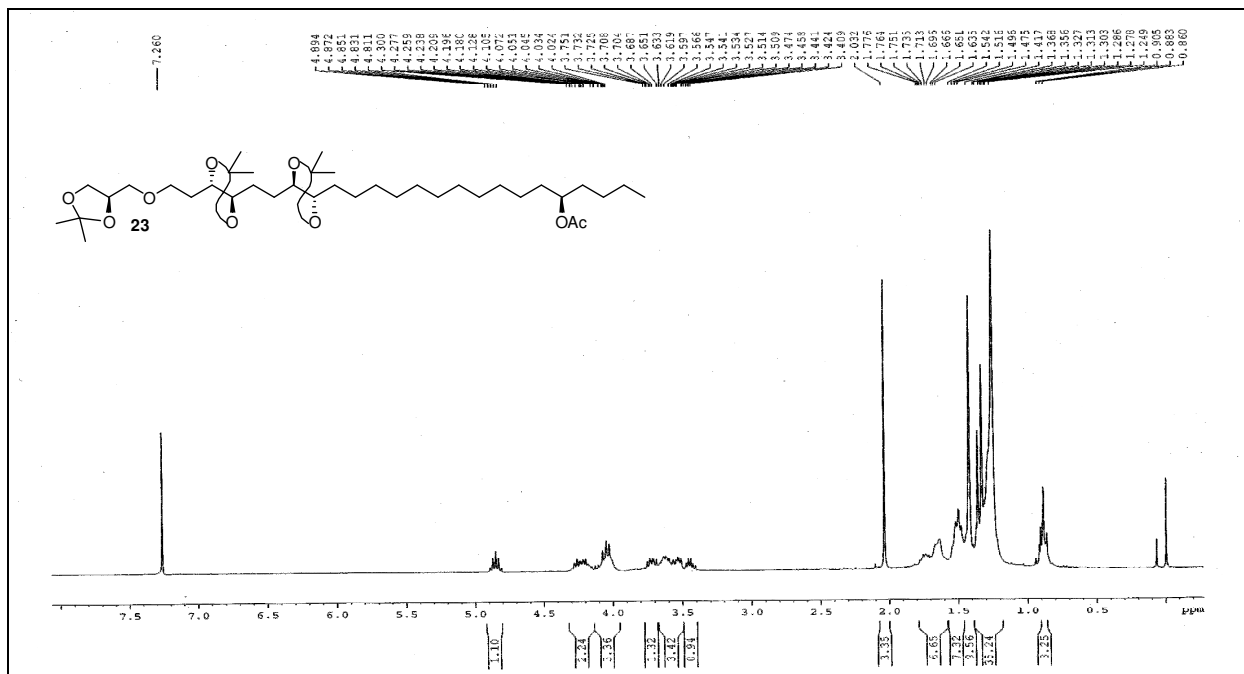
^1H NMR spectrum of 41 (a-d) (300 MHz, CDCl_3):



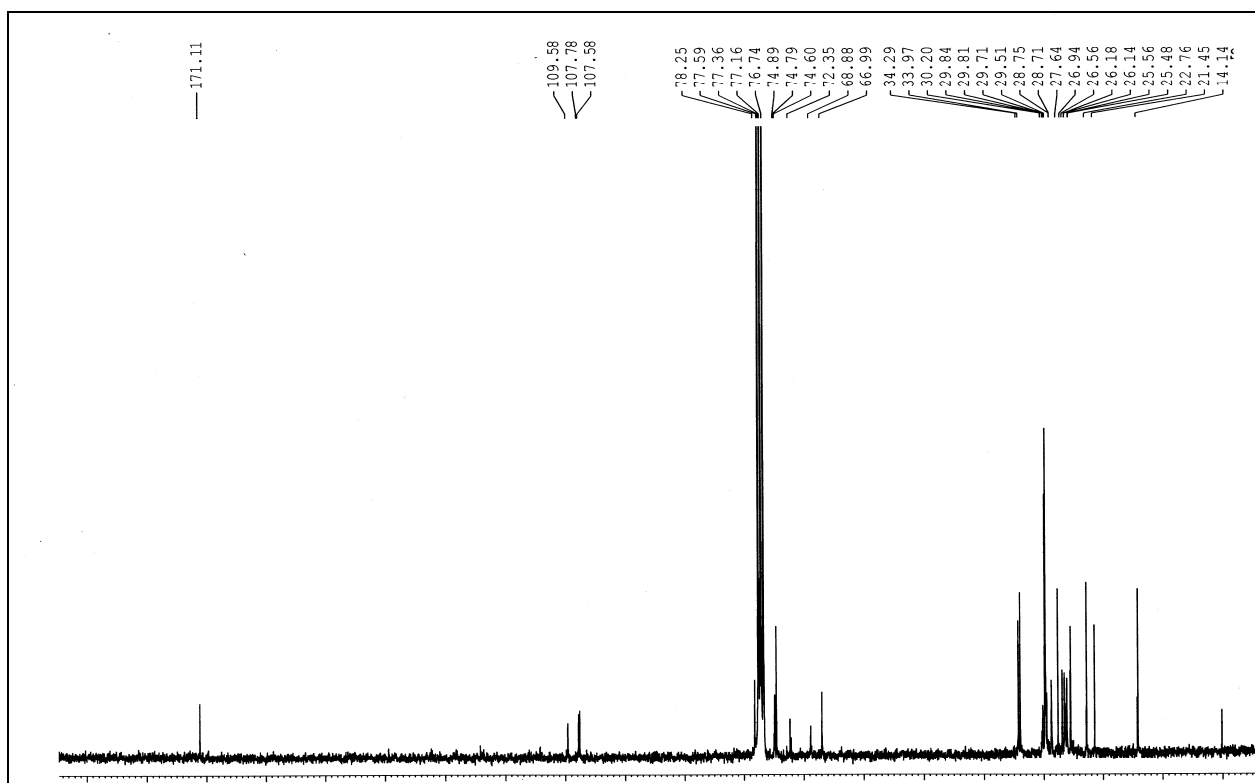
^{13}C NMR spectrum of 41 (a-d) (75 MHz, CDCl_3):



^1H NMR spectrum of 23 (300 MHz, CDCl_3):



^{13}C NMR spectrum of 23 (75 MHz, CDCl_3):



Chemical structure of **42(a-d)** is shown above the spectrum. The structure is a complex molecule featuring a central carbon-carbon double bond, multiple oxygen atoms, and a long alkyl chain with a terminal acetoxy group (AcO).

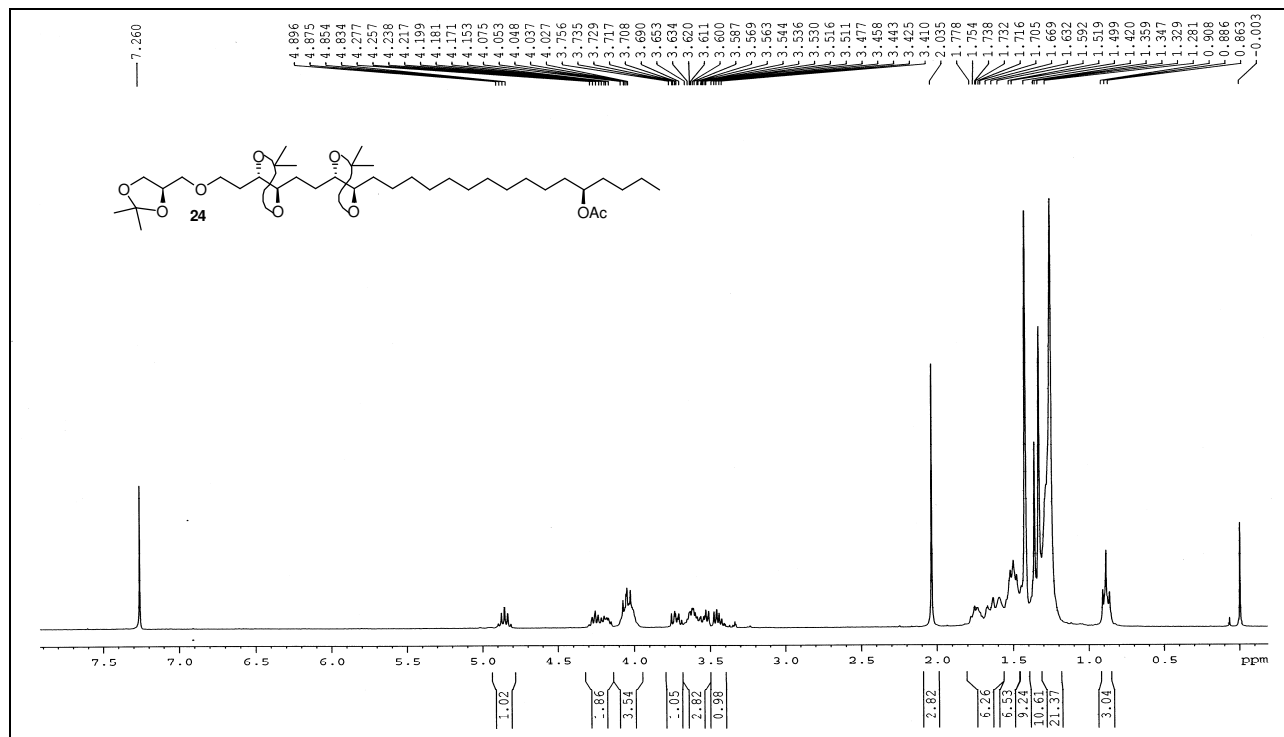
The ¹H NMR spectrum (CDCl₃) displays the following chemical shifts (ppm) and integrations:

Chemical Shift (ppm)	Integration
7.260, 7.247, 7.232, 7.218, 7.188, 7.163, 7.143, 7.123, 7.107, 7.091, 7.075, 7.059, 7.043, 7.027, 7.011, 7.000, 6.984, 6.968, 6.952, 6.936, 6.920, 6.904, 6.888, 6.871, 6.855, 6.839, 6.823, 6.807, 6.791, 6.775, 6.759, 6.743, 6.727, 6.711, 6.695, 6.679, 6.663, 6.647, 6.631, 6.615, 6.599, 6.583, 6.567, 6.551, 6.535, 6.519, 6.503, 6.487, 6.471, 6.455, 6.439, 6.423, 6.407, 6.391, 6.375, 6.359, 6.343, 6.327, 6.311, 6.295, 6.279, 6.263, 6.247, 6.231, 6.215, 6.199, 6.183, 6.167, 6.151, 6.135, 6.119, 6.103, 6.087, 6.071, 6.055, 6.039, 6.023, 6.007, 5.991, 5.975, 5.959, 5.943, 5.927, 5.911, 5.895, 5.879, 5.863, 5.847, 5.831, 5.815, 5.799, 5.783, 5.767, 5.751, 5.735, 5.719, 5.703, 5.687, 5.671, 5.655, 5.639, 5.623, 5.607, 5.591, 5.575, 5.559, 5.543, 5.527, 5.511, 5.495, 5.479, 5.463, 5.447, 5.431, 5.415, 5.399, 5.383, 5.367, 5.351, 5.335, 5.319, 5.303, 5.287, 5.271, 5.255, 5.239, 5.223, 5.207, 5.191, 5.175, 5.159, 5.143, 5.127, 5.111, 5.095, 5.079, 5.063, 5.047, 5.031, 5.015, 4.999, 4.983, 4.967, 4.951, 4.935, 4.919, 4.903, 4.887, 4.871, 4.855, 4.839, 4.823, 4.807, 4.791, 4.775, 4.759, 4.743, 4.727, 4.711, 4.695, 4.679, 4.663, 4.647, 4.631, 4.615, 4.599, 4.583, 4.567, 4.551, 4.535, 4.519, 4.503, 4.487, 4.471, 4.455, 4.439, 4.423, 4.407, 4.391, 4.375, 4.359, 4.343, 4.327, 4.311, 4.295, 4.279, 4.263, 4.247, 4.231, 4.215, 4.199, 4.183, 4.167, 4.151, 4.135, 4.119, 4.103, 4.087, 4.071, 4.055, 4.039, 4.023, 4.007, 3.991, 3.975, 3.959, 3.943, 3.927, 3.911, 3.895, 3.879, 3.863, 3.847, 3.831, 3.815, 3.799, 3.783, 3.767, 3.751, 3.735, 3.719, 3.703, 3.687, 3.671, 3.655, 3.639, 3.623, 3.607, 3.591, 3.575, 3.559, 3.543, 3.527, 3.511, 3.495, 3.479, 3.463, 3.447, 3.431, 3.415, 3.399, 3.383, 3.367, 3.351, 3.335, 3.319, 3.303, 3.287, 3.271, 3.255, 3.239, 3.223, 3.207, 3.191, 3.175, 3.159, 3.143, 3.127, 3.111, 3.095, 3.079, 3.063, 3.047, 3.031, 3.015, 2.999, 2.983, 2.967, 2.951, 2.935, 2.919, 2.903, 2.887, 2.871, 2.855, 2.839, 2.823, 2.807, 2.791, 2.775, 2.759, 2.743, 2.727, 2.711, 2.695, 2.679, 2.663, 2.647, 2.631, 2.615, 2.599, 2.583, 2.567, 2.551, 2.535, 2.519, 2.503, 2.487, 2.471, 2.455, 2.439, 2.423, 2.407, 2.391, 2.375, 2.359, 2.343, 2.327, 2.311, 2.295, 2.279, 2.263, 2.247, 2.231, 2.215, 2.199, 2.183, 2.167, 2.151, 2.135, 2.119, 2.103, 2.087, 2.071, 2.055, 2.039, 2.023, 2.007, 1.991, 1.975, 1.959, 1.943, 1.927, 1.911, 1.895, 1.879, 1.863, 1.847, 1.831, 1.815, 1.799, 1.783, 1.767, 1.751, 1.735, 1.719, 1.703, 1.687, 1.671, 1.655, 1.639, 1.623, 1.607, 1.591, 1.575, 1.559, 1.543, 1.527, 1.511, 1.495, 1.479, 1.463, 1.447, 1.431, 1.415, 1.399, 1.383, 1.367, 1.351, 1.335, 1.319, 1.303, 1.287, 1.271, 1.255, 1.239, 1.223, 1.207, 1.191, 1.175, 1.159, 1.143, 1.127, 1.111, 1.095, 1.079, 1.063, 1.047, 1.031, 1.015, 0.999, 0.983, 0.967, 0.951, 0.935, 0.919, 0.903, 0.887, 0.871, 0.855, 0.839, 0.823, 0.807, 0.791, 0.775, 0.759, 0.743, 0.727, 0.711, 0.695, 0.679, 0.663, 0.647, 0.631, 0.615, 0.599, 0.583, 0.567, 0.551, 0.535, 0.519, 0.503, 0.487, 0.471, 0.455, 0.439, 0.423, 0.407, 0.391, 0.375, 0.359, 0.343, 0.327, 0.311, 0.295, 0.279, 0.263, 0.247, 0.231, 0.215, 0.199, 0.183, 0.167, 0.151, 0.135, 0.119, 0.103, 0.087, 0.071, 0.055, 0.039, 0.023, 0.007, -0.007	1.13, 2.90, 1.00, 1.06, 1.98, 2.09, 1.05, 1.15, 3.04, 1.08, 2.09, 3.18, 3.27, 12.20, 6.09, 7.57, 12.65, 3.50

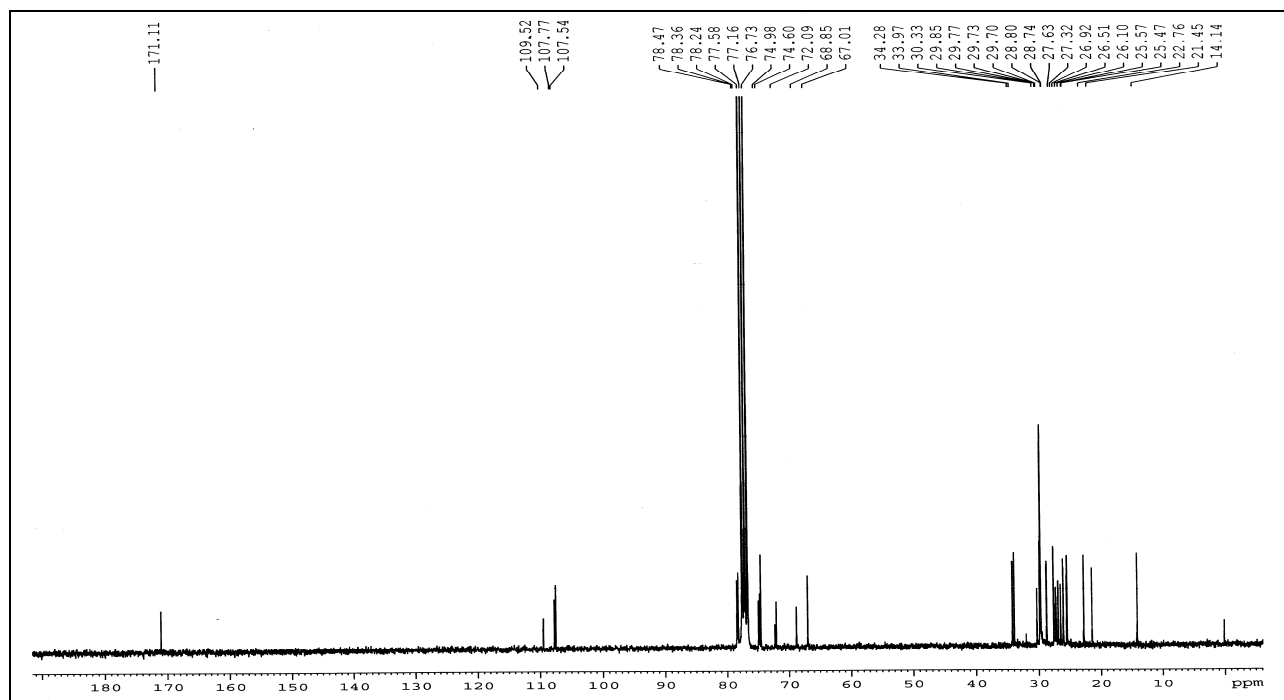
Chemical shifts (ppm) labeled on the spectrum:

- 171.07
- 136.73
- 130.05
- 129.15
- 113.77
- 109.48
- 109.35
- 108.64
- 97.22
- 77.58
- 77.16
- 76.73
- 76.40
- 75.72
- 74.83
- 74.75
- 74.48
- 73.75
- 72.25
- 72.09
- 68.94
- 67.04
- 54.26
- 33.97
- 31.18
- 29.60
- 29.21
- 28.09
- 28.85
- 28.51
- 28.30
- 27.62
- 26.92
- 25.89
- 25.65
- 25.54
- 25.47
- 22.74
- 21.43
- 19.68
- 14.13

^1H NMR spectrum of 24 (300 MHz, CDCl_3):



^{13}C NMR spectrum of 24 (75 MHz, CDCl_3):



[illegible]

154.15
133.33
131.36
129.36
125.92
109.48
109.26
77.58
77.16
76.73
75.84
74.47
72.54
72.40
68.23
66.57
58.43
29.65
27.57
26.31
25.53
25.26

[illegible]

154.21
133.45
131.43
129.43
125.99
109.62
109.36
77.58
77.16
76.74
75.83
74.59
72.67
72.63
68.23
66.76
58.53
29.75
27.64
26.93
25.60
25.33

Chemical structure of **49(a-d)** is shown above the spectrum. The structure is a symmetrical molecule consisting of two identical units linked by a central double bond. Each unit features a cyclohexene ring with a tert-butyl group and a side chain containing an ether linkage and a methyl group.

¹H NMR spectrum (CDCl₃) of **49(a-d)** is displayed below the structure. The x-axis represents the chemical shift in ppm, ranging from 0 to 8.5. The spectrum shows several peaks corresponding to the protons in the molecule, with integration values provided below the baseline.

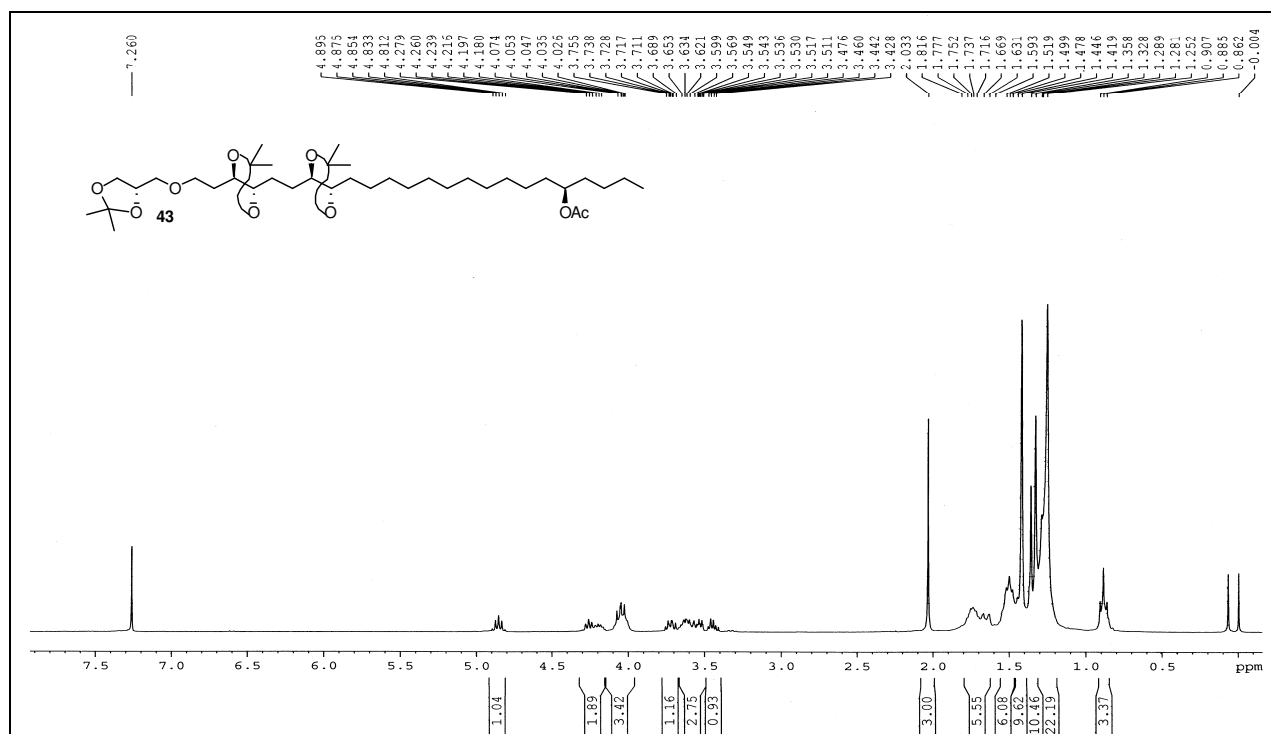
Chemical shift (ppm) values (from left to right): 7.261, 6.513, 6.510, 6.502, 6.499, 6.487, 6.484, 6.476, 6.473, 6.470, 6.468, 6.273, 6.266, 6.247, 6.240, 5.639, 5.601, 5.593, 5.584, 5.575, 5.569, 5.531, 5.521, 5.498, 5.486, 5.076, 5.063, 5.052, 4.944, 4.944, 4.923, 4.919, 4.906, 4.898, 4.879, 4.854, 4.841, 4.822, 4.273, 4.263, 4.254, 4.243, 4.231, 4.220, 4.211, 4.211, 4.199, 4.076, 4.054, 4.054, 4.016, 3.756, 3.734, 3.728, 3.711, 3.707, 3.606, 3.597, 3.585, 3.574, 3.563, 3.554, 3.535, 3.515, 3.502, 3.485, 3.447, 3.432, 3.414, 1.681, 1.659, 1.635, 1.613, 1.514, 1.462, 1.419, 1.411, 1.358.

Integration values (from left to right): 1.00, 1.03, 2.05, 1.04, 2.24, 2.29, 1.27, 1.20, 3.61, 1.21, 3.53, 3.53, 3.53, 3.53, 8.35.

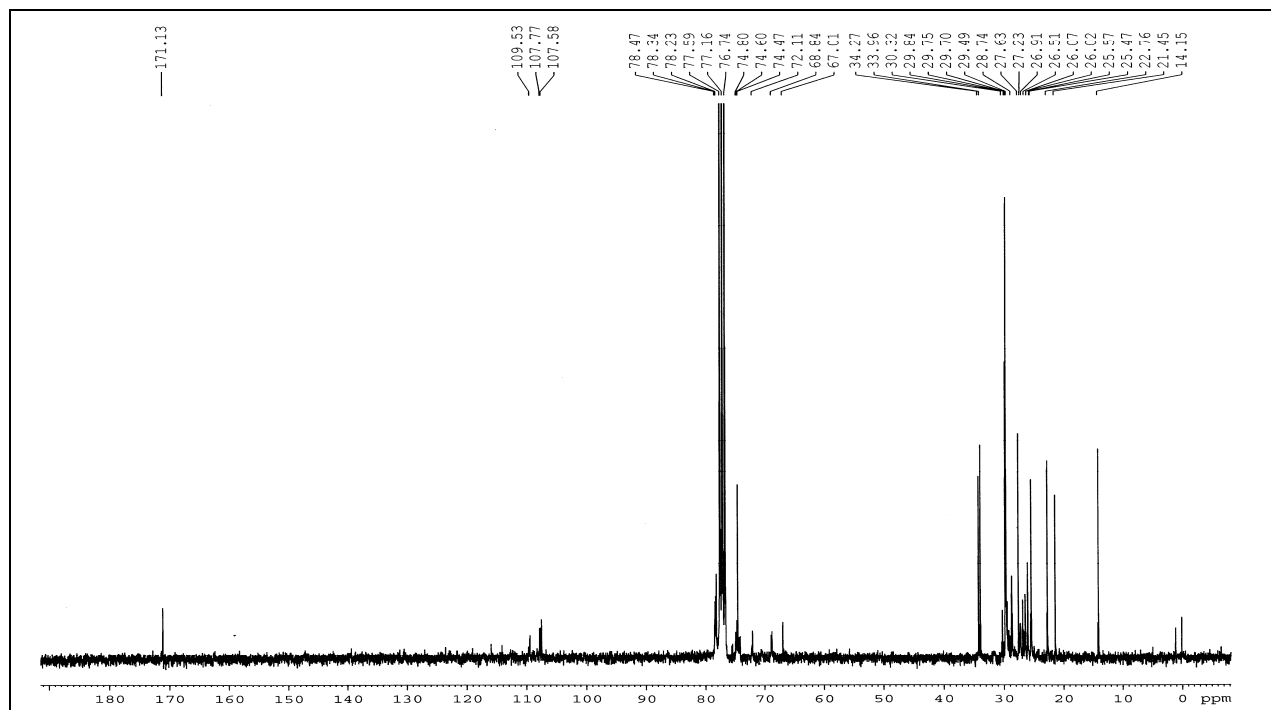
Chemical shifts (ppm) labeled on the spectrum:

- 136.38
- 138.92
- 138.08
- 108.31
- 108.58
- 108.52
- 107.76
- 84.70
- 80.42
- 76.58
- 76.16
- 75.74
- 74.67
- 73.77
- 72.94
- 72.77
- 71.14
- 67.83
- 66.04
- 30.33
- 28.64
- 27.48
- 27.20
- 25.66
- 24.88
- 24.69
- 24.54

¹H NMR spectrum of 43 (300 MHz, CDCl₃):



^{13}C NMR spectrum of 43 (75 MHz, CDCl_3):



Chemical structure of **50(a-d)** is shown above the spectrum. The structure is a complex molecule featuring a central carbon-carbon double bond, two quaternary carbon atoms, and two ether linkages. The molecule is labeled **50(a-d)**.

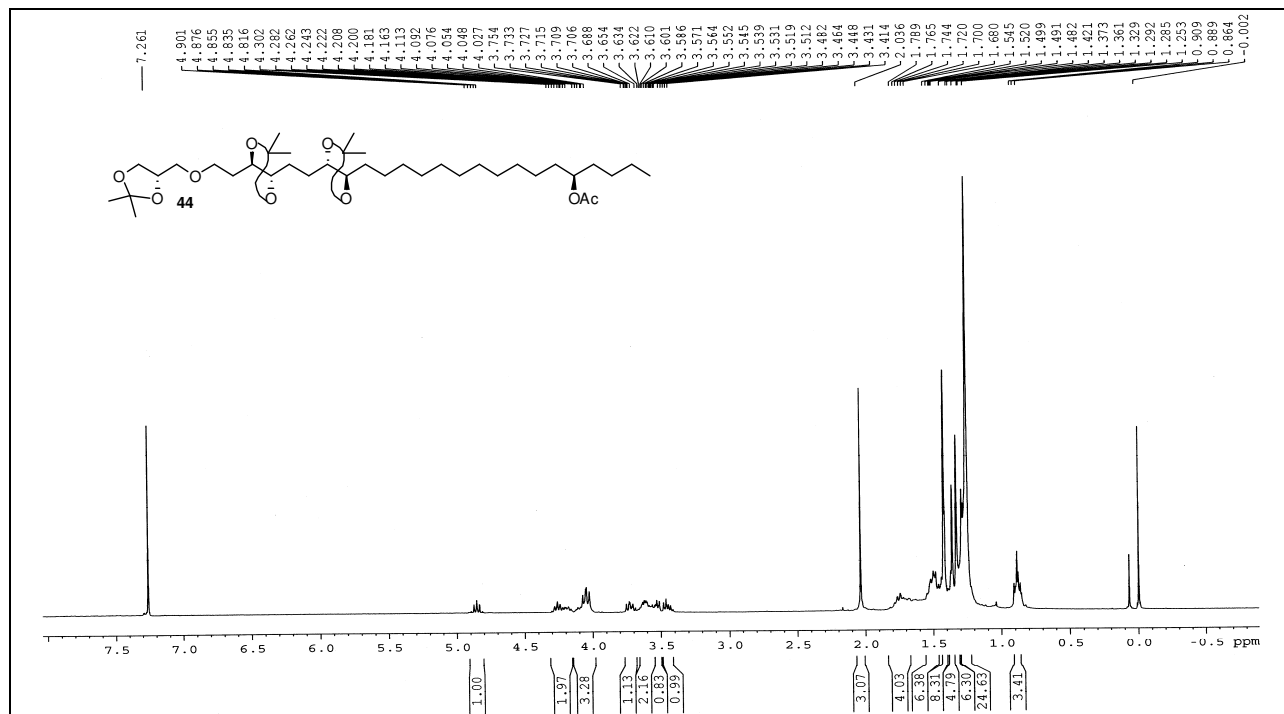
¹H NMR spectrum (CDCl₃) of **50(a-d)**. The x-axis represents the chemical shift in ppm, ranging from 0 to 8.5. The spectrum shows several peaks, with integration values provided below the baseline. The peaks are labeled with their corresponding chemical shifts (ppm) on the right side of the spectrum.

Chemical shift (ppm): 7.260, 6.510, 6.507, 6.500, 6.497, 6.485, 6.482, 6.474, 6.471, 6.298, 6.292, 6.271, 6.245, 6.238, 5.638, 5.599, 5.591, 5.582, 5.567, 5.529, 5.506, 5.474, 5.451, 5.442, 4.922, 4.917, 4.906, 4.896, 4.877, 4.852, 4.829, 4.801, 4.790, 4.280, 4.270, 4.261, 4.241, 4.220, 4.197, 4.074, 4.052, 4.047, 4.025, 3.754, 3.743, 3.732, 3.727, 3.710, 3.705, 3.694, 3.683, 3.635, 3.623, 3.604, 3.584, 3.572, 3.562, 3.552, 3.533, 3.519, 3.500, 3.463, 3.445, 3.430, 3.412, 3.397, 1.680, 1.657, 1.634, 1.612, 1.513, 1.460, 1.411, 1.402, 1.356, -0.005.

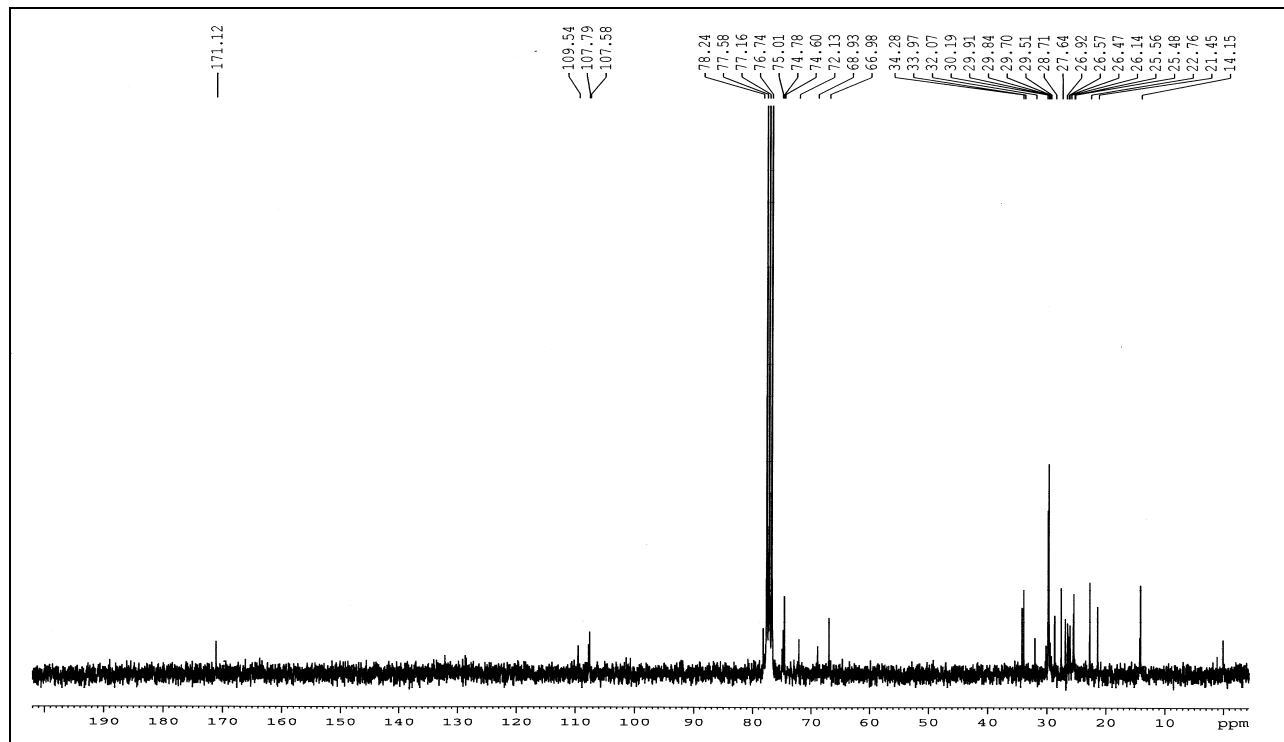
Integration values (from left to right): 1.00, 1.09, 2.08, 1.00, 2.26, 2.29, 1.37, 1.50, 3.73, 1.40, 3.56, 3.86, 2.94, 6.68, 6.88.

Chemical Shift (ppm)
137.39
129.93
129.10
109.95
109.82
108.77
85.69
81.43
77.58
77.16
76.74
75.68
75.61
74.52
74.78
73.55
73.78
72.36
72.16
68.85
67.05
31.34
29.84
28.49
28.21
26.97
25.88
25.82
25.70
25.55

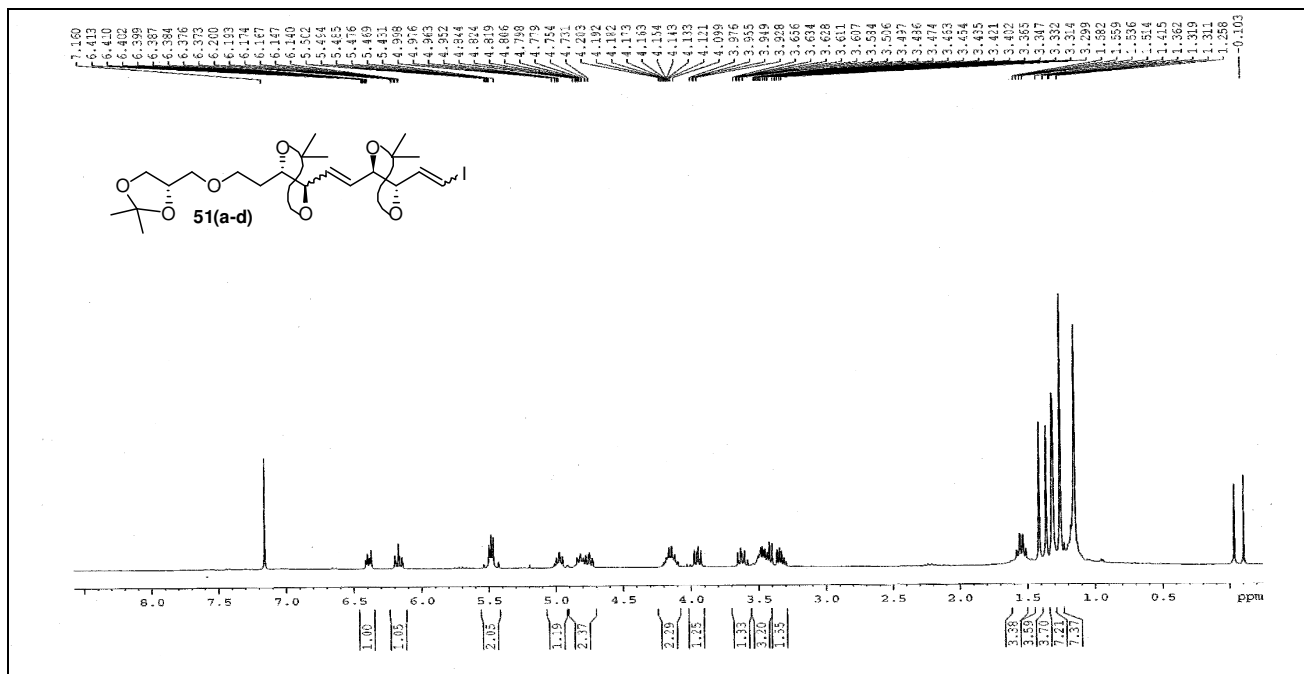
^1H NMR spectrum of 44 (300 MHz, CDCl_3):



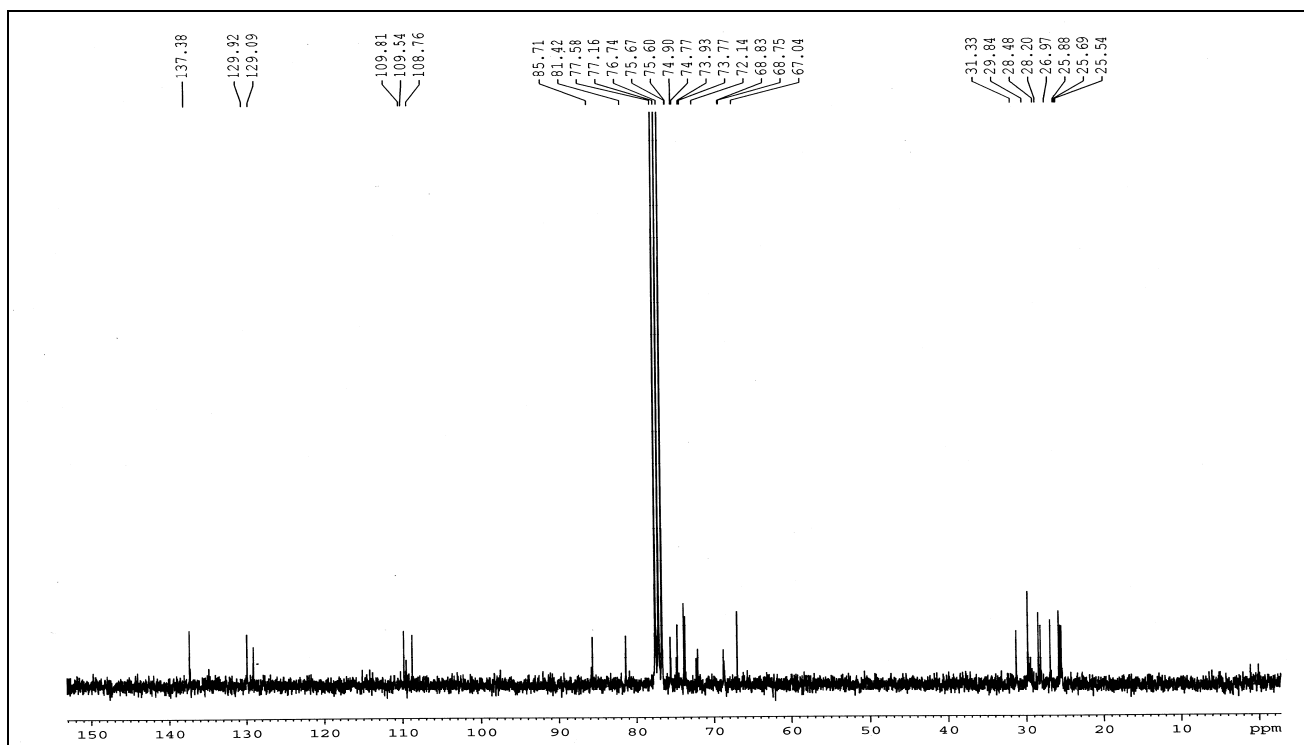
^{13}C NMR spectrum of 44 (75 MHz, CDCl_3):



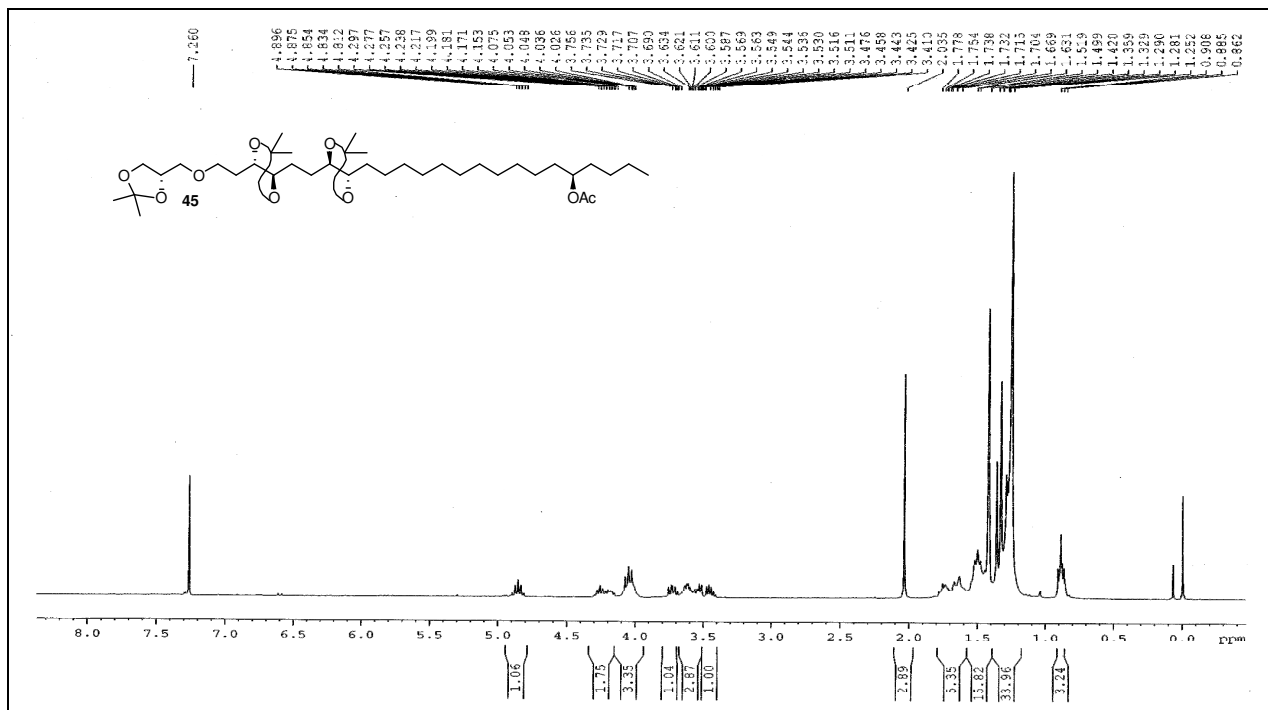
¹H NMR spectrum of 51 (a-d) (300 MHz, CDCl₃):



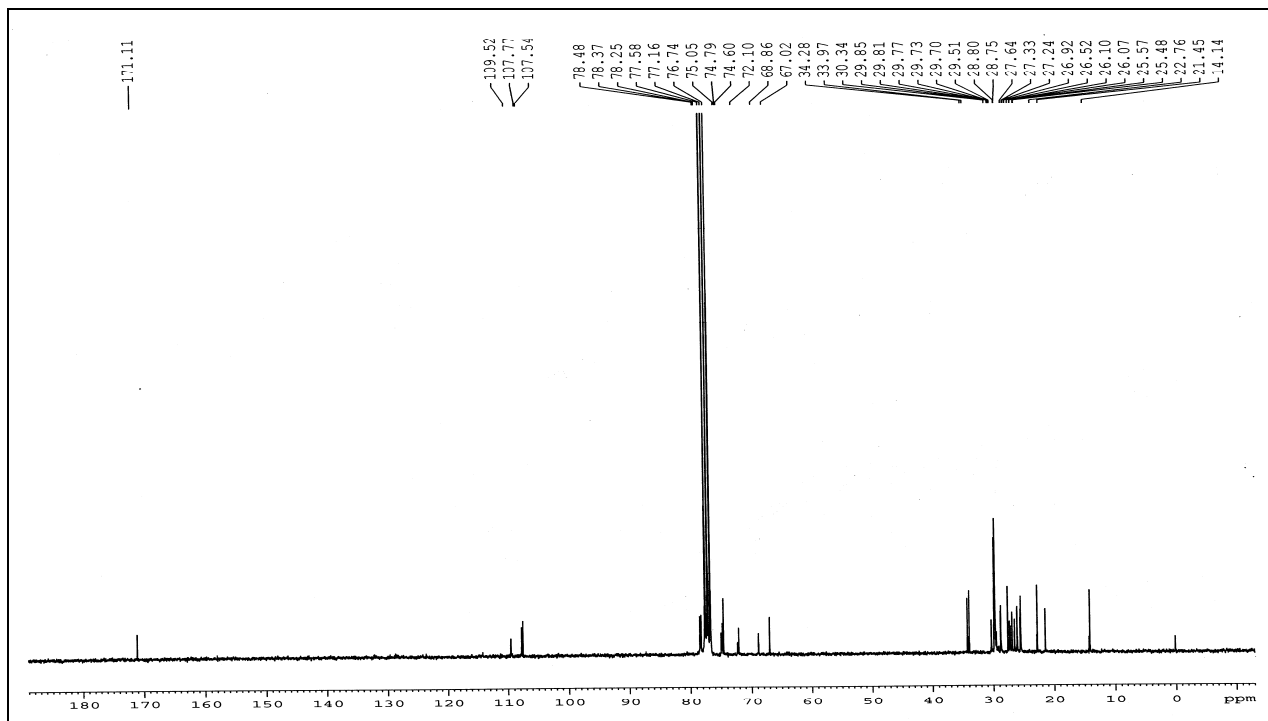
¹³C NMR spectrum of 51 (a-d) (75 MHz, CDCl₃):



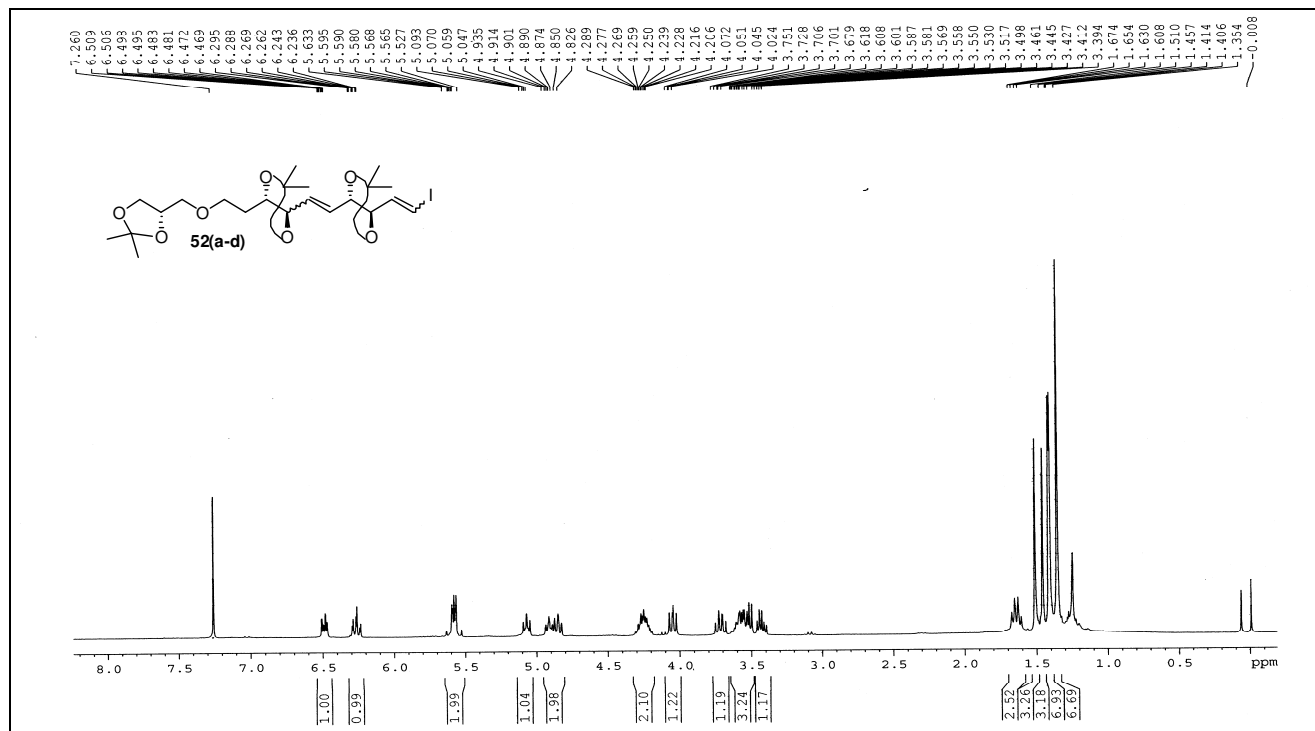
^1H NMR spectrum of 45 (300 MHz, CDCl_3):



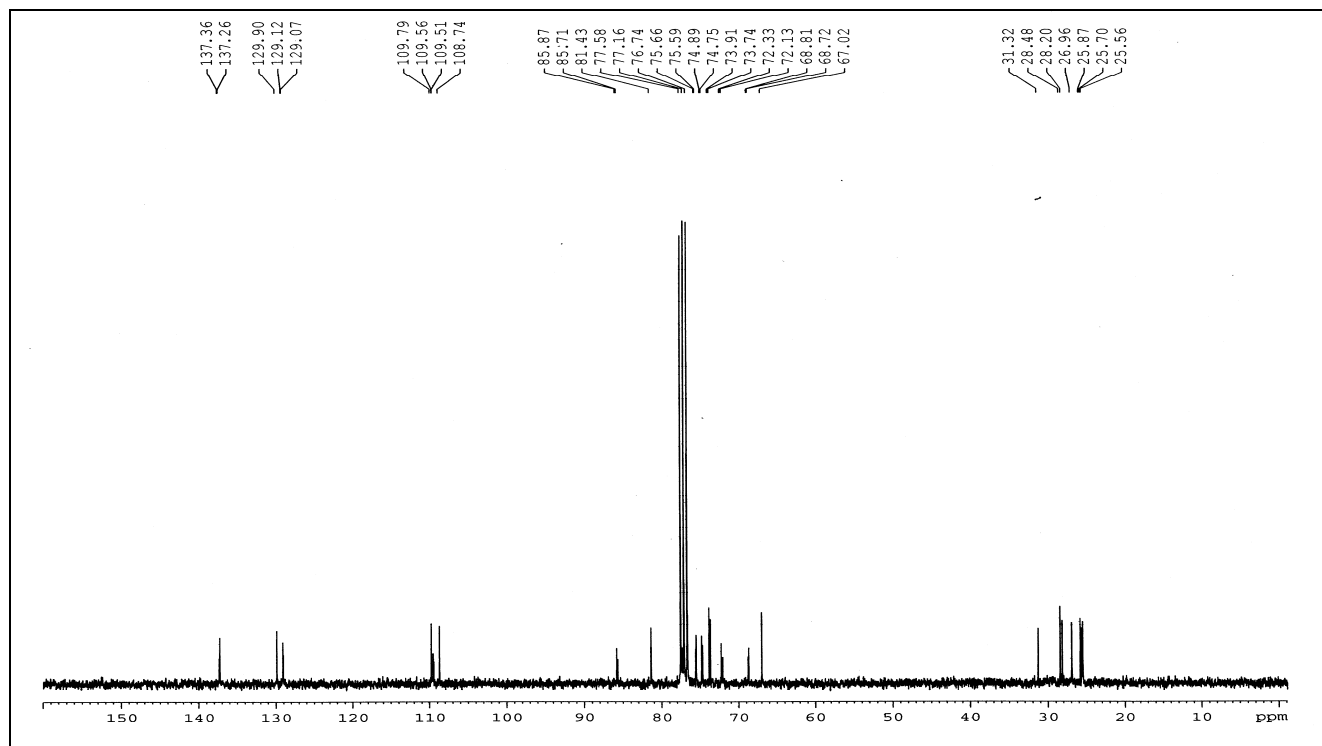
^{13}C NMR spectrum of 45 (75 MHz, CDCl_3):



^1H NMR spectrum of 52 (a-d) (300 MHz, CDCl_3):



^{13}C NMR spectrum of 52 (a-d) (75 MHz, CDCl_3):



[illegible]

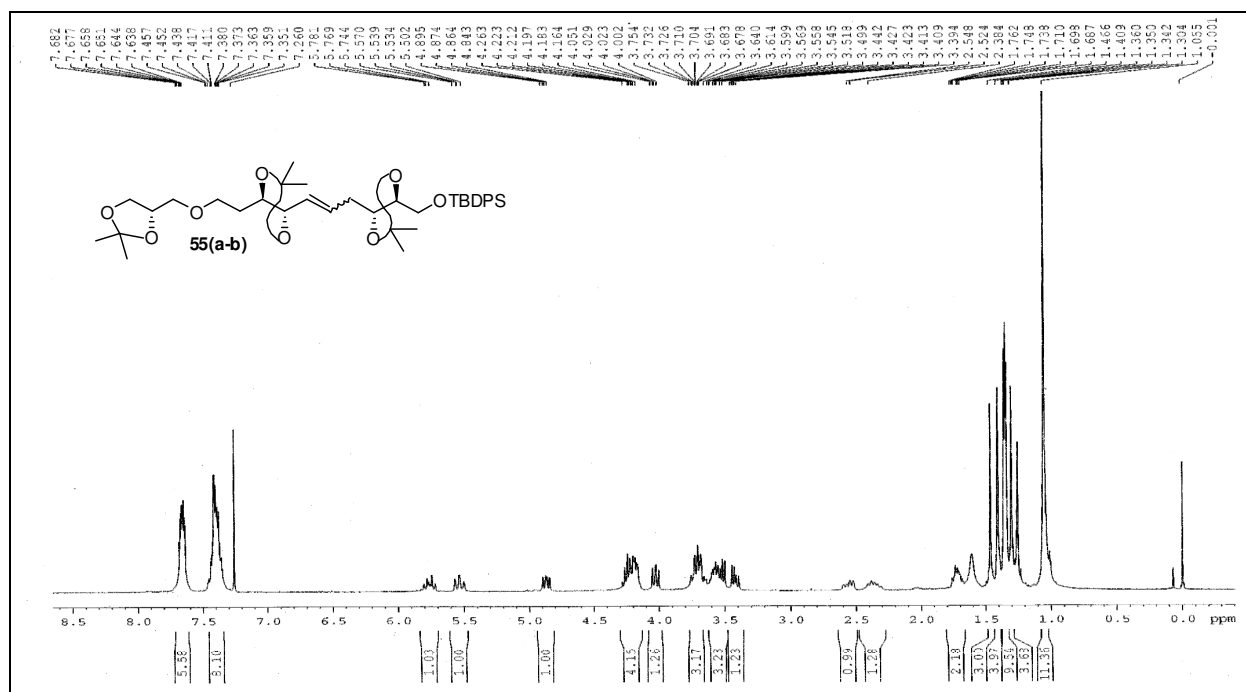
171.09

109.58
107.75
107.53

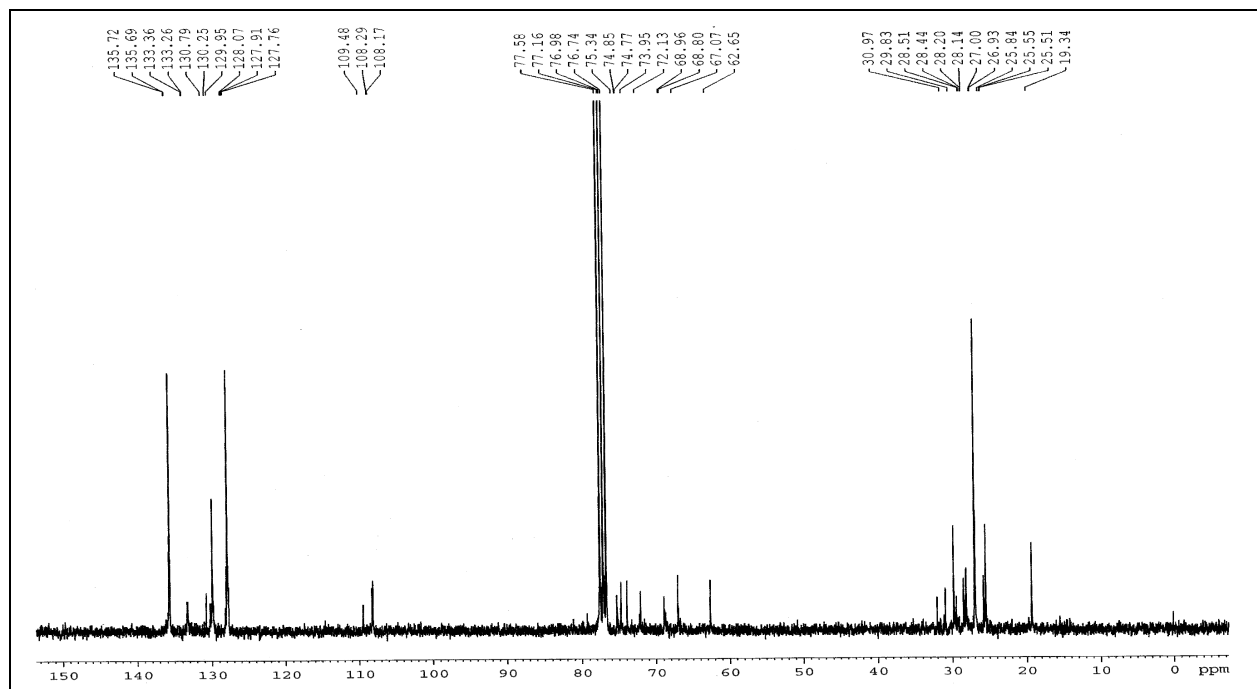
78.47
78.36
78.23
77.58
77.16
76.74
74.82
74.87
74.58
72.31
68.82
67.01
34.28
33.96
33.96
30.33
29.84
29.79
29.76
29.72
29.70
29.50
28.79
27.32
26.93
26.51
26.09
26.06
25.56
25.47
22.75
21.44
14.14

ppm

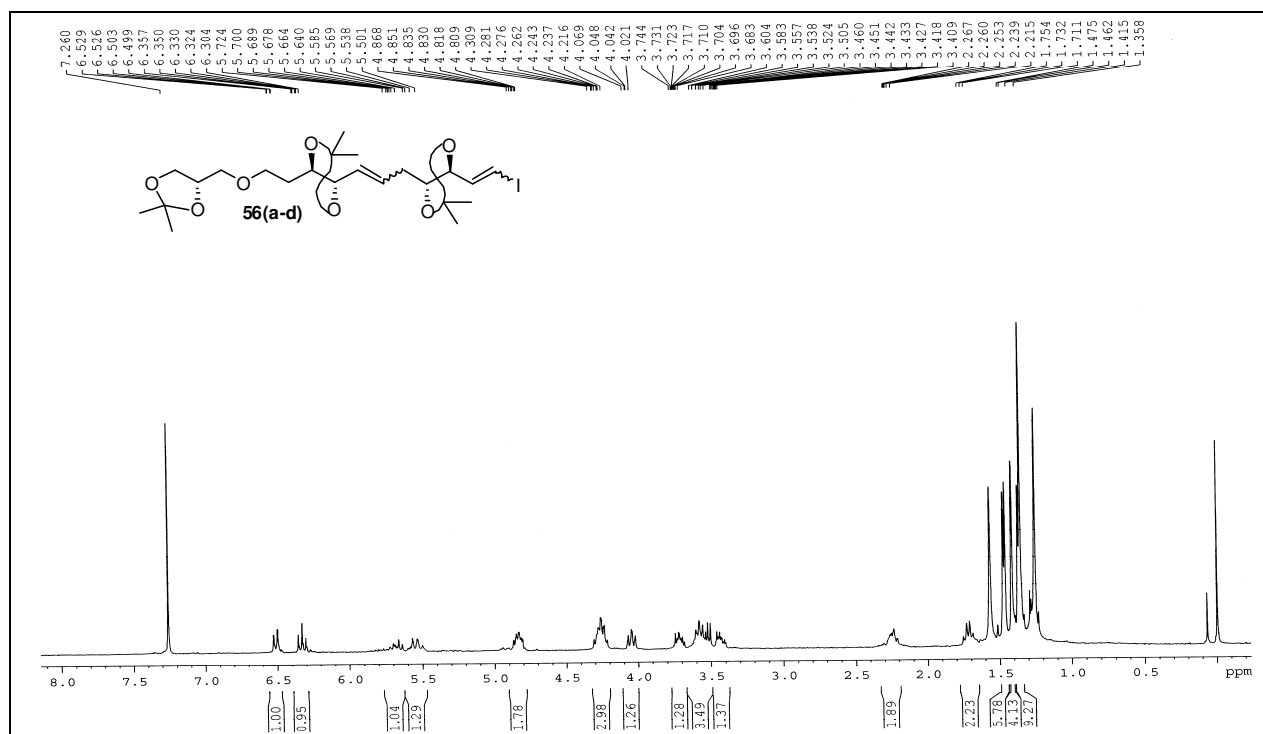
^1H NMR spectrum of 55 (a-b) (300 MHz, CDCl_3):



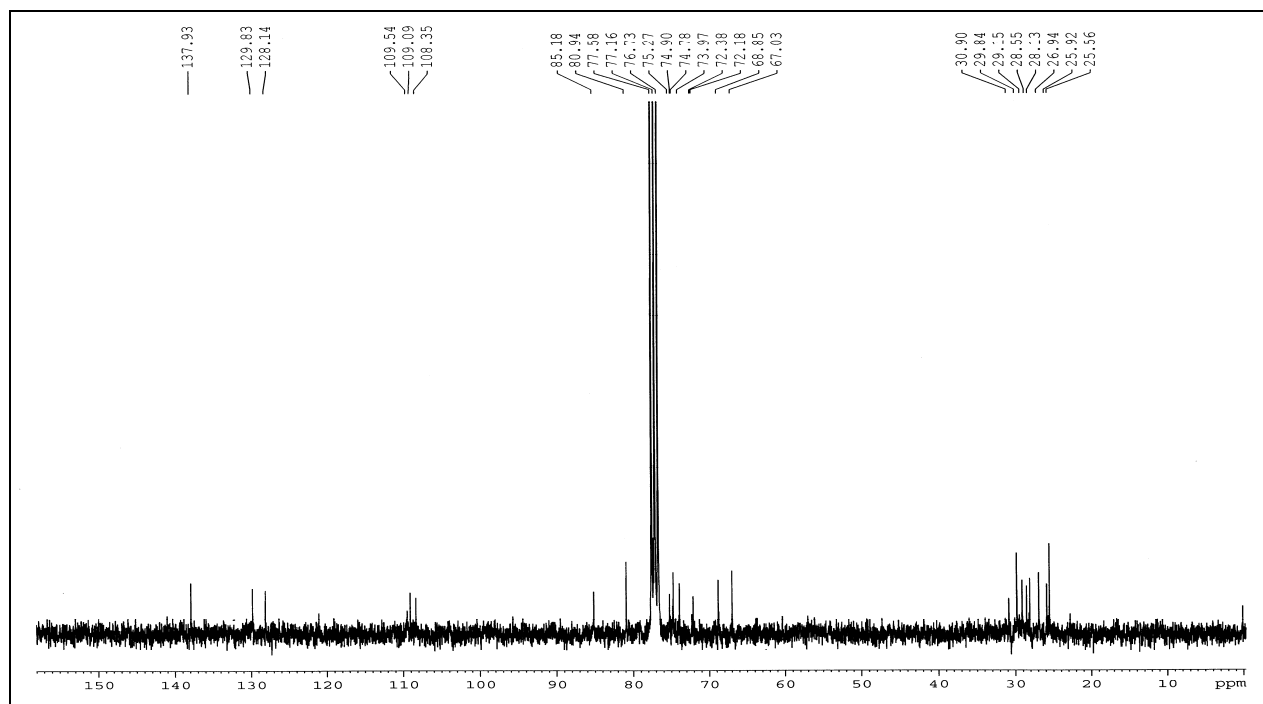
^{13}C NMR spectrum of 55 (a-b) (75 MHz, CDCl_3):



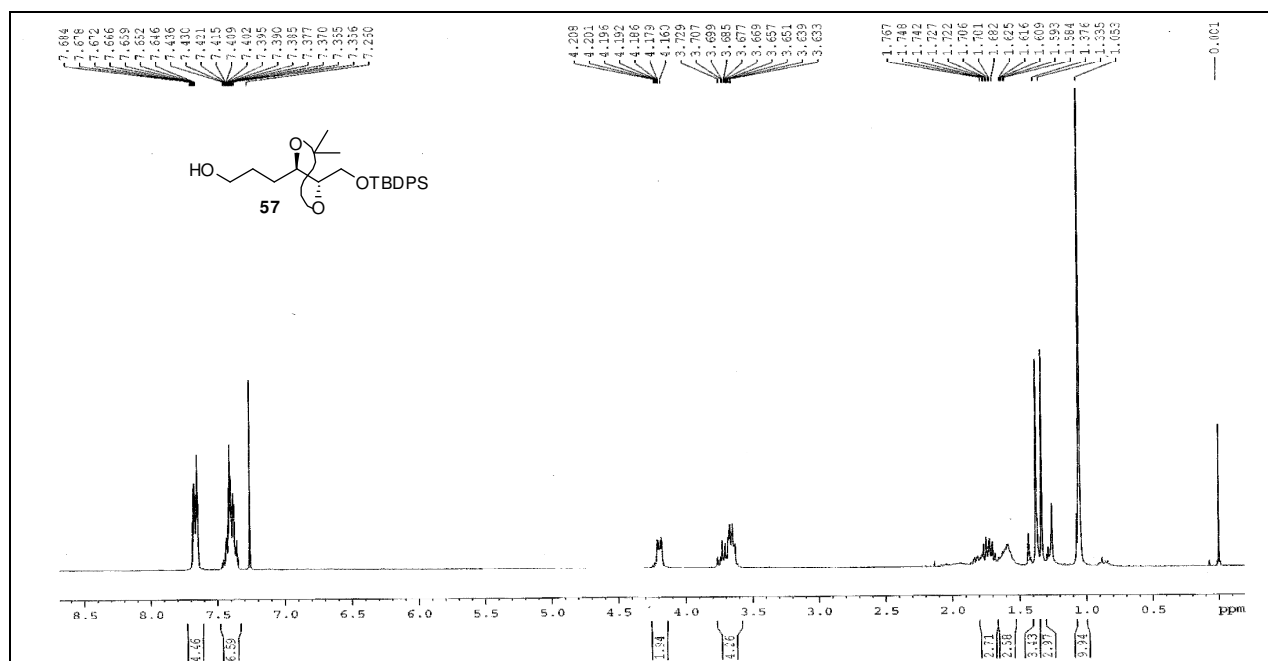
¹H NMR spectrum of 56 (a-d) (300 MHz, CDCl₃):



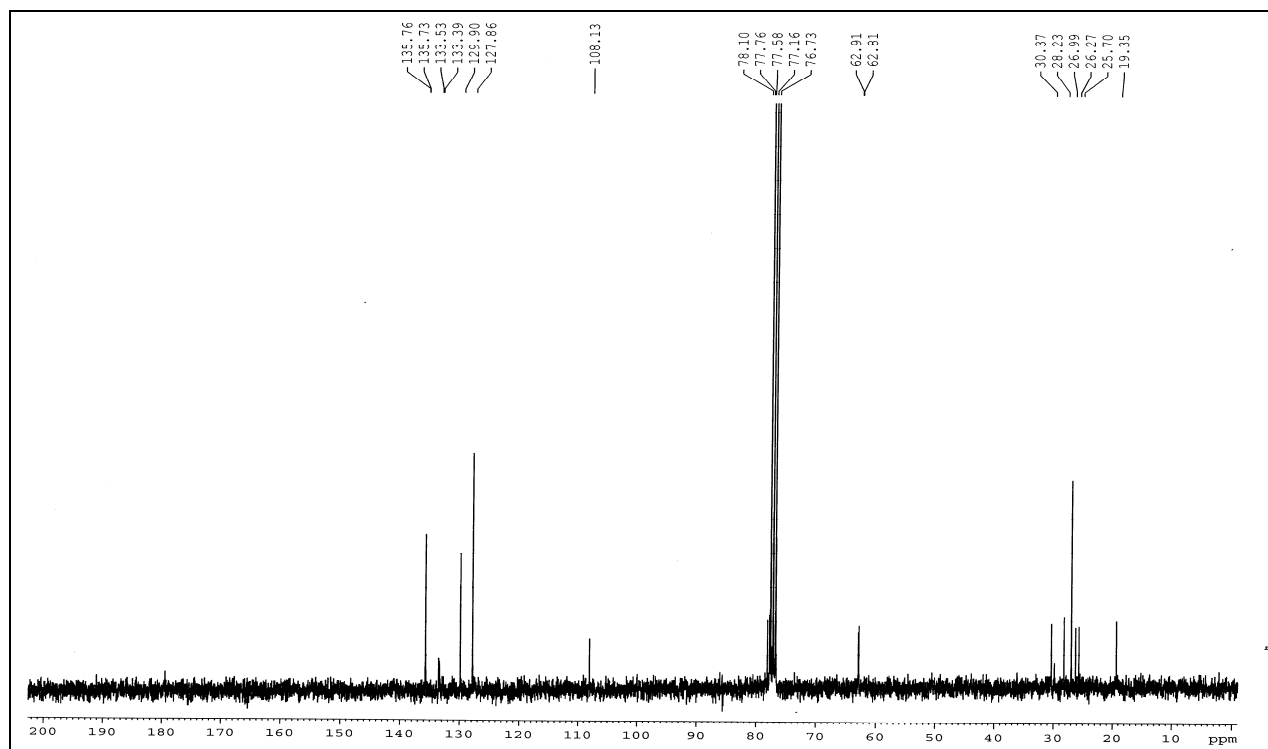
^{13}C NMR spectrum of 56 (a-d) (75 MHz, CDCl_3):



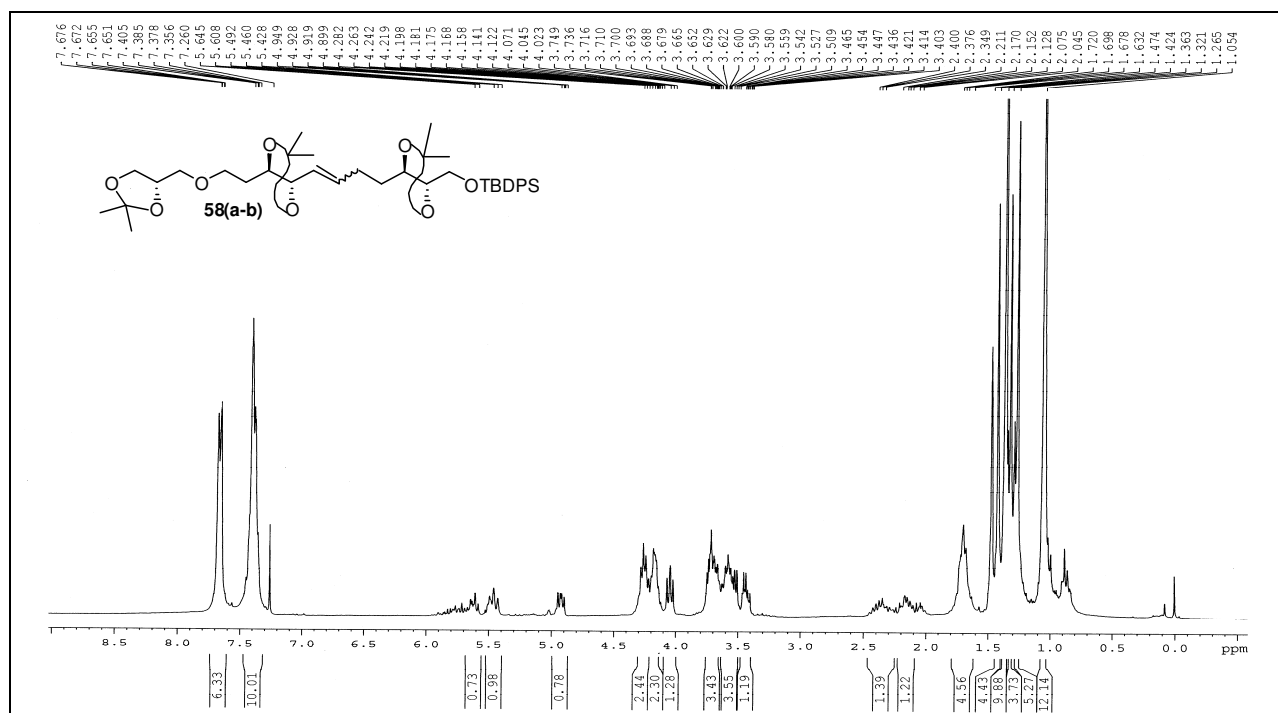
^1H NMR spectrum of 57 (300 MHz, CDCl_3):



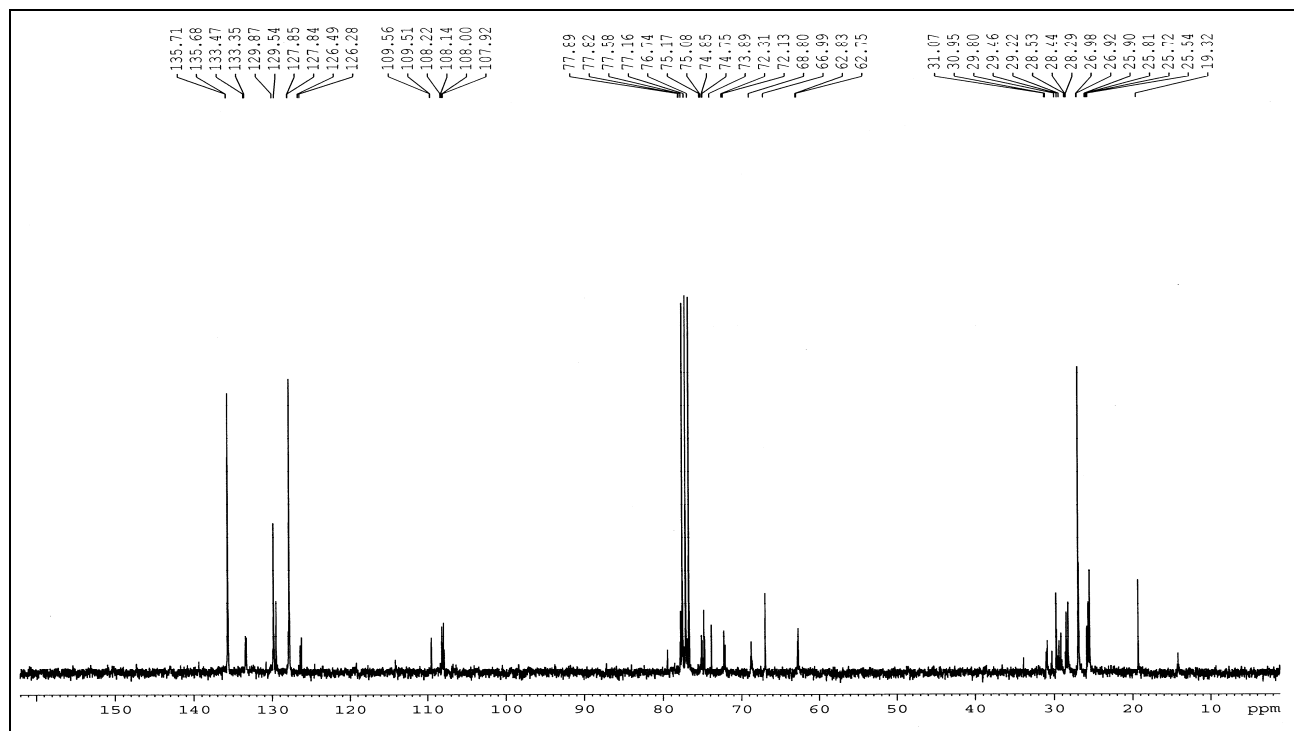
^{13}C NMR spectrum of 57 (75 MHz, CDCl_3):



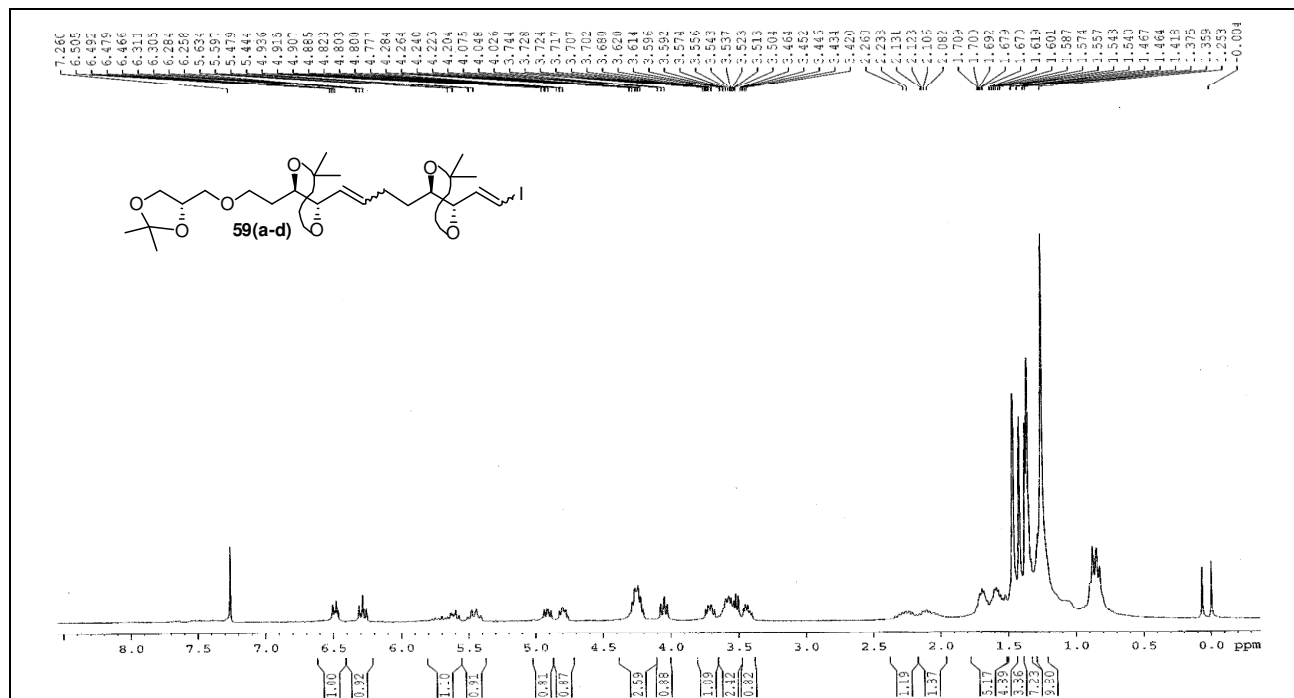
^1H NMR spectrum of 58 (a-b) (300 MHz, CDCl_3):



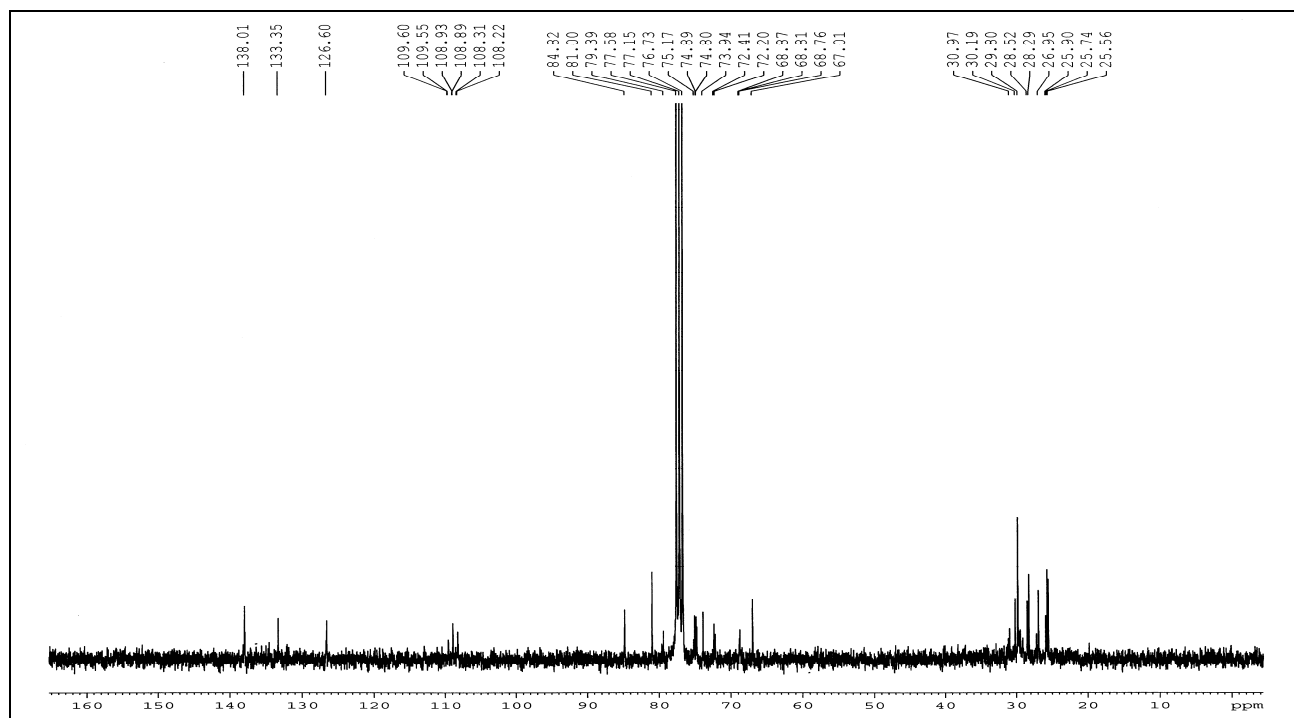
^{13}C NMR spectrum of 58 (a-b) (75 MHz, CDCl_3):



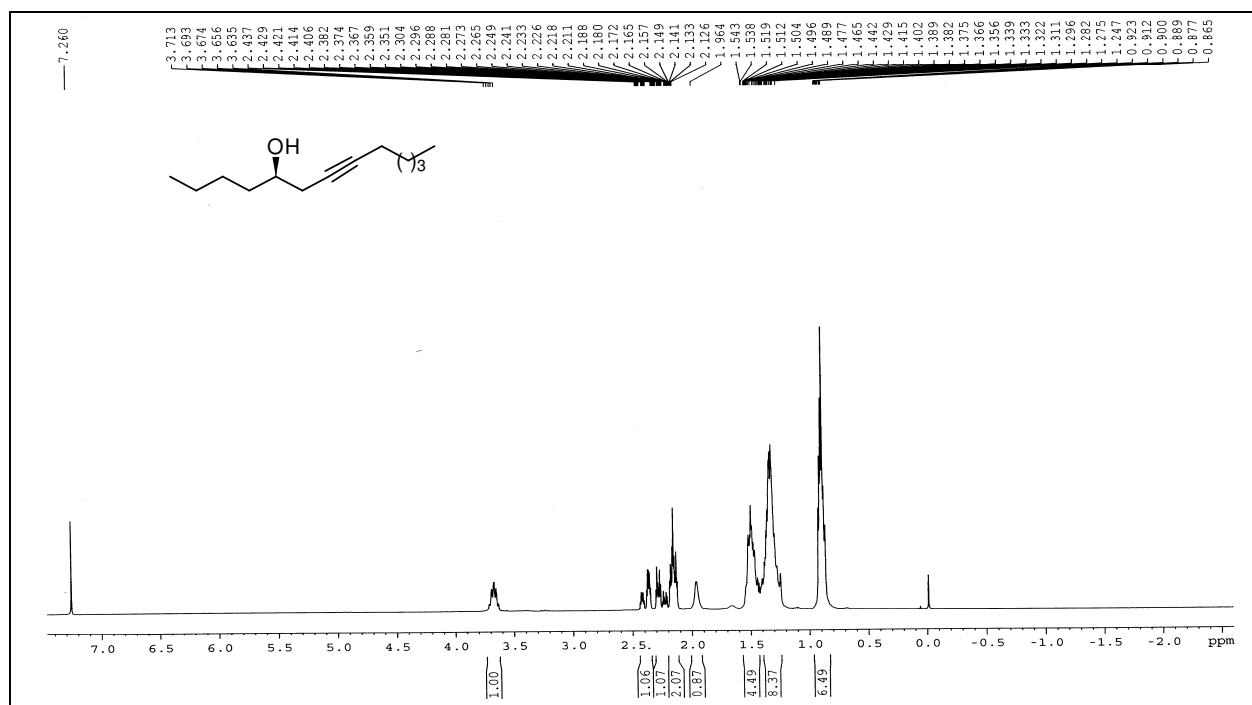
^1H NMR spectrum of 59 (a-d) (300 MHz, CDCl_3):



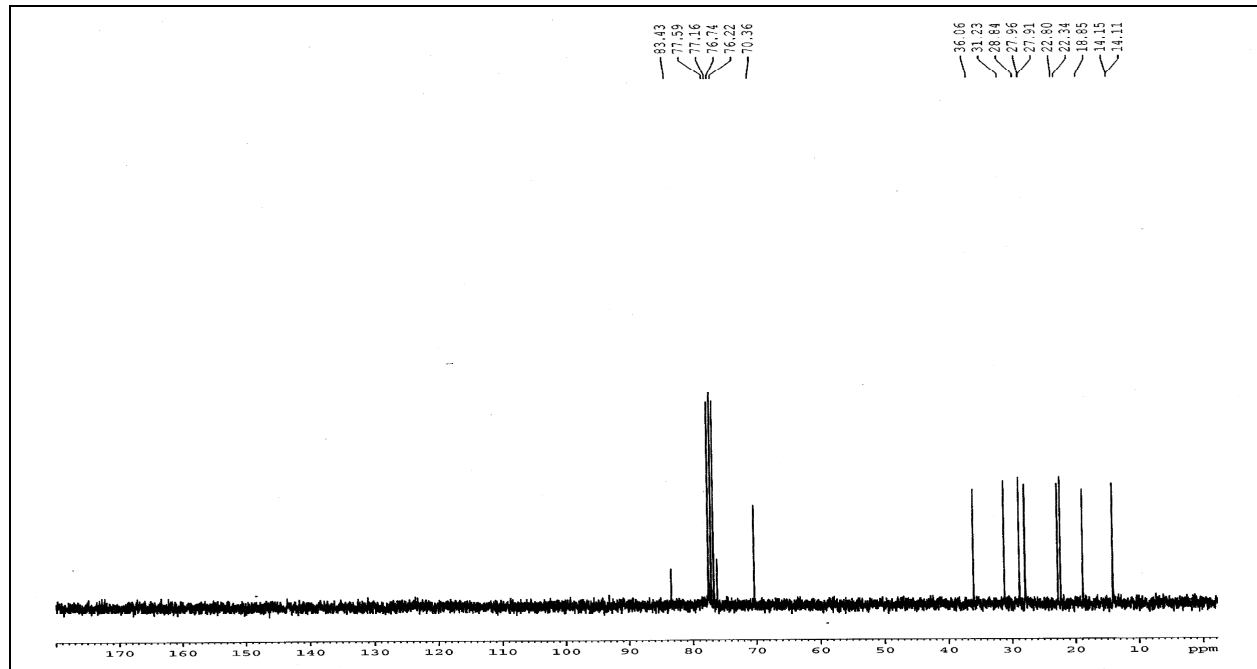
^{13}C NMR spectrum of 59 (a-b) (75 MHz, CDCl_3):



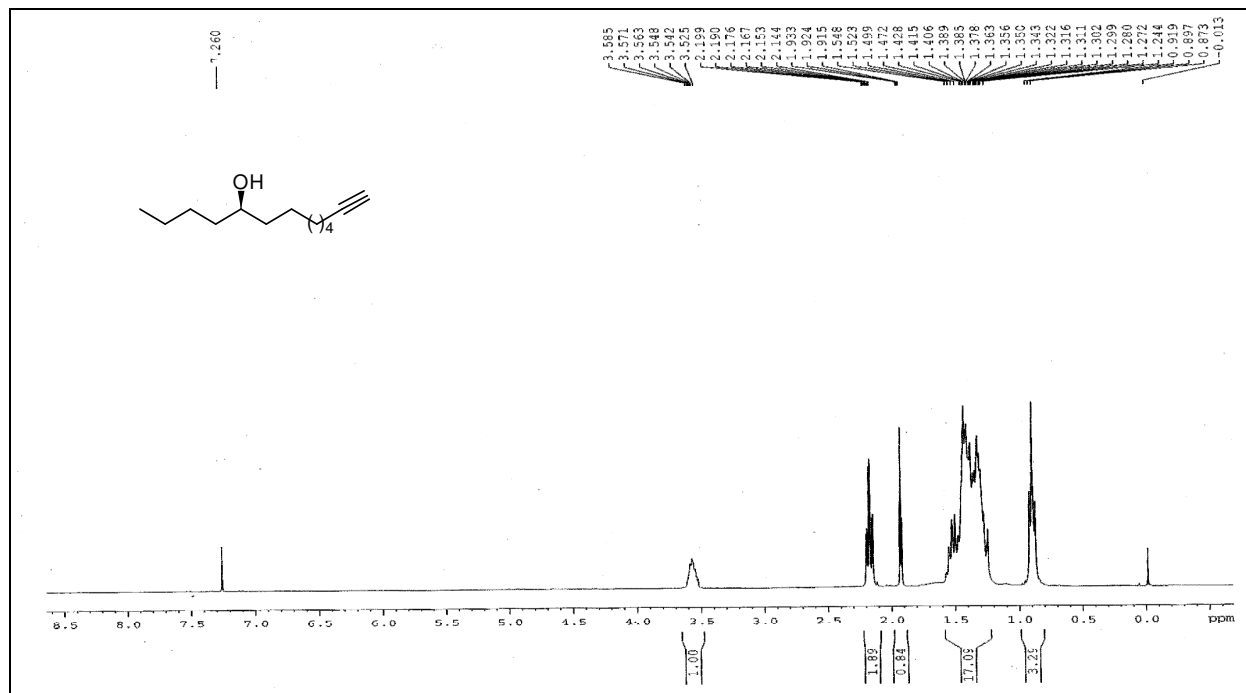
^1H NMR spectrum of 60a (300 MHz, CDCl_3):



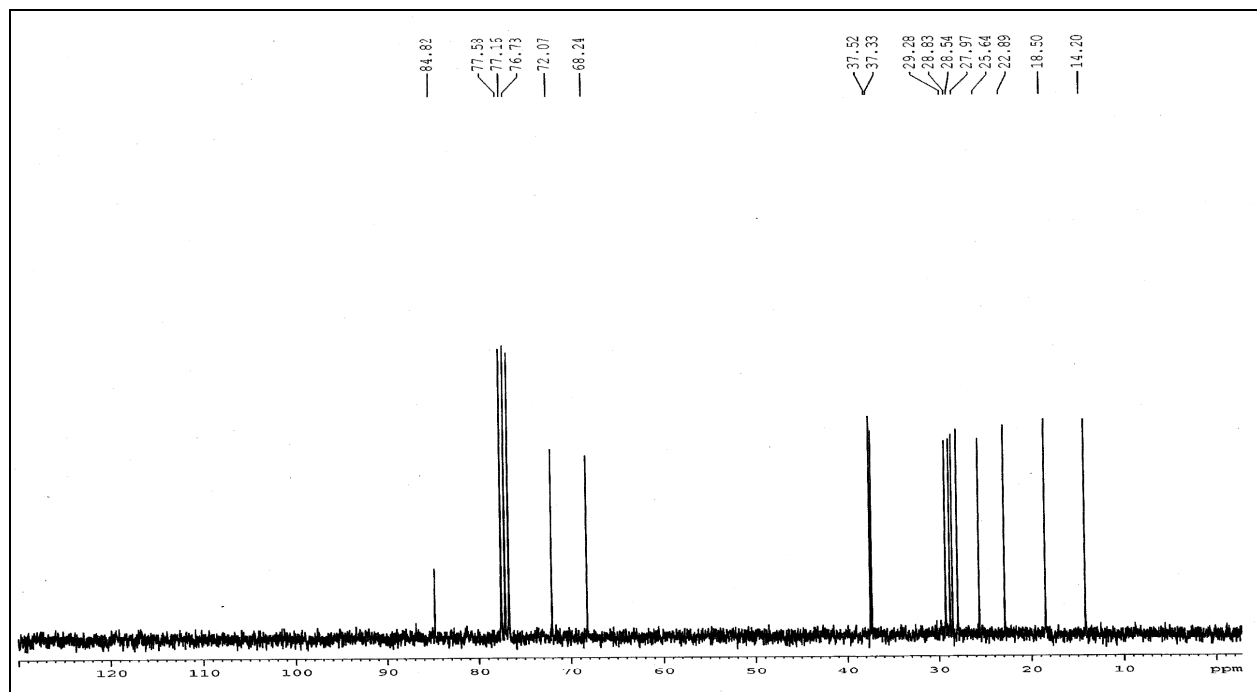
^{13}C NMR spectrum of 60a (75 MHz, CDCl_3):



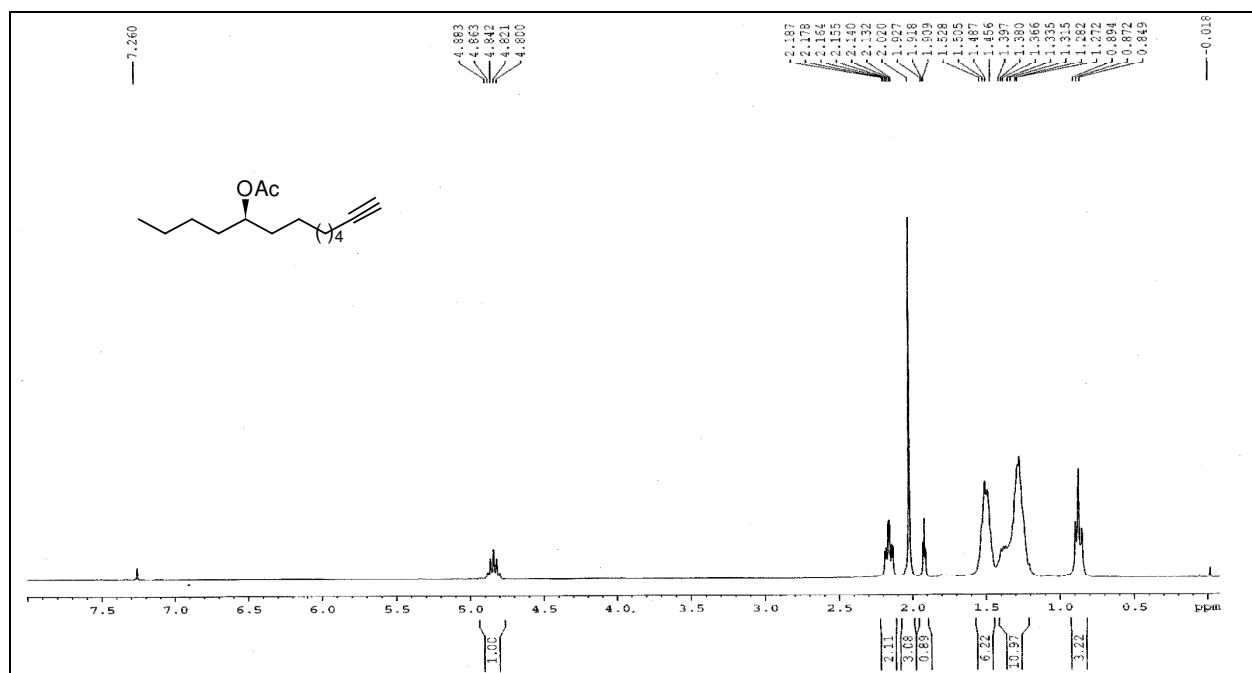
^1H NMR spectrum of 61a (300 MHz, CDCl_3):



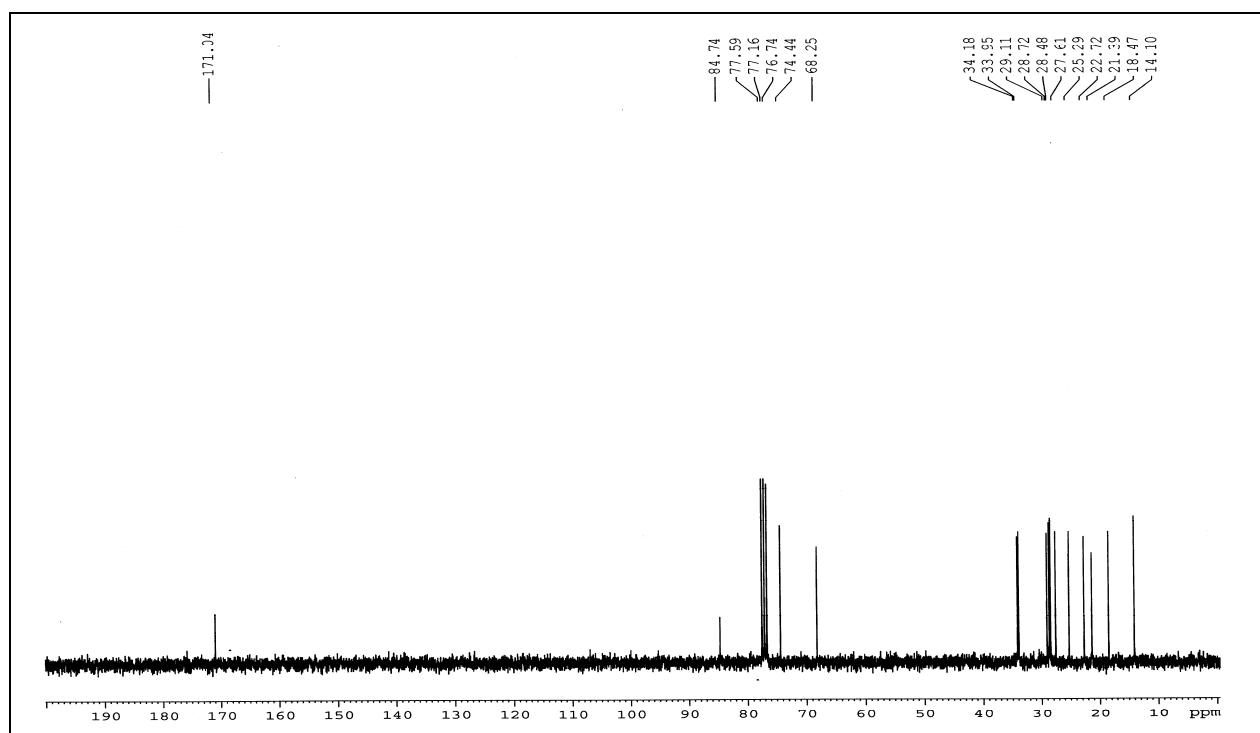
^{13}C NMR spectrum of 61a (75 MHz, CDCl_3):



¹H NMR spectrum of 62a (300 MHz, CDCl₃):



¹³C NMR spectrum of 62a (75 MHz, CDCl₃):

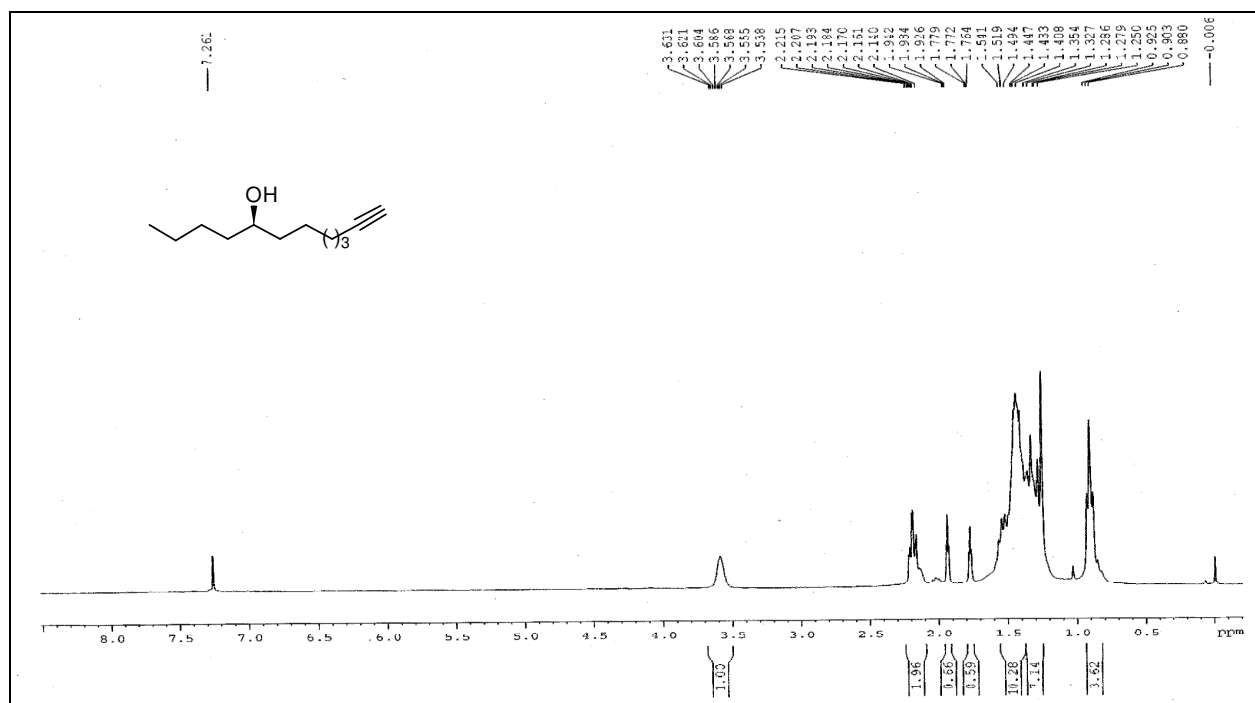


CCCC[C@H](O)CC#C

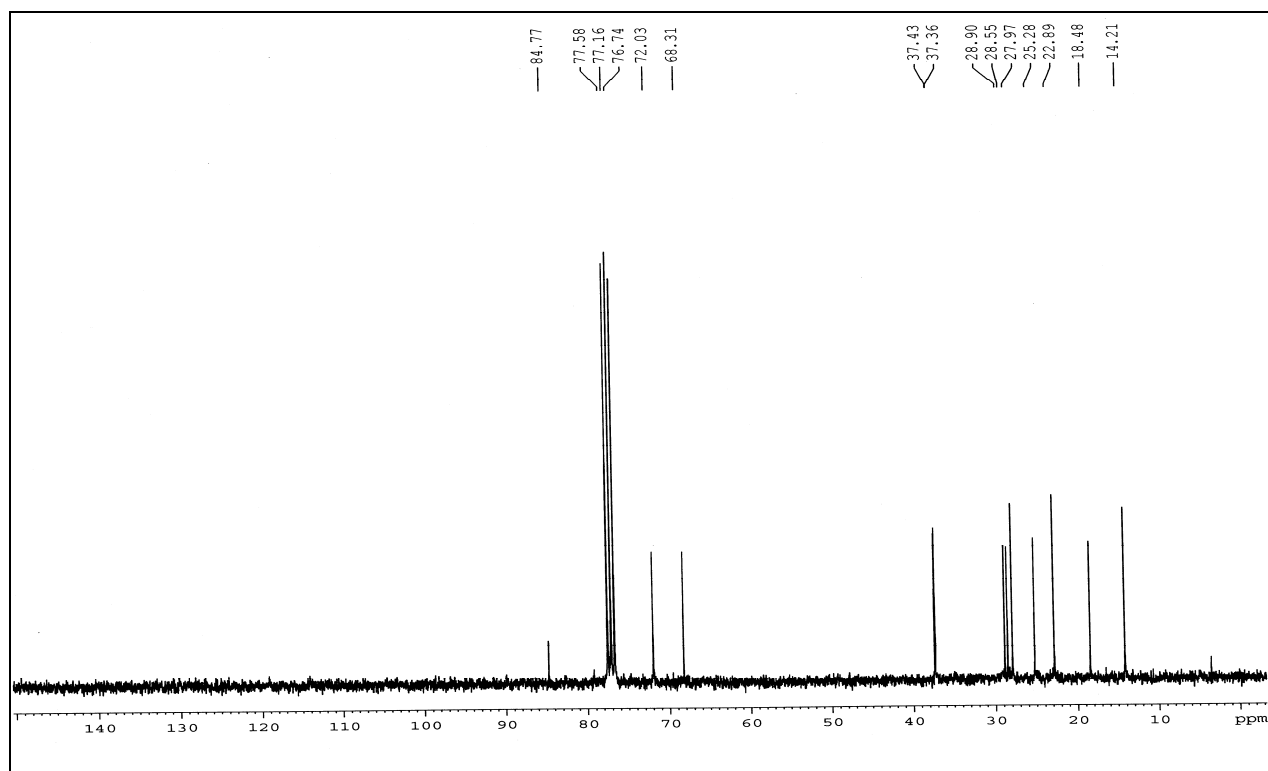
Chemical Shift (ppm)	Integration
~7.26	-
~3.70 - 3.87	1.00
~2.10 - 2.30	1.06 1.13 1.06 1.97
~1.40 - 1.60	1.35
~0.90 - 1.10	6.52

13C NMR spectrum (CDCl₃) of compound 1. The x-axis represents chemical shift in ppm, ranging from 140 to 10. The spectrum shows several sharp peaks. A cluster of peaks is visible between 70 and 85 ppm, and another cluster is visible between 15 and 35 ppm. The peaks are labeled with their chemical shift values: 83.33, 77.59, 77.16, 76.74, 76.21, 70.35, 36.04, 31.21, 27.94, 22.78, 22.07, 16.55, 14.13, and 13.71.

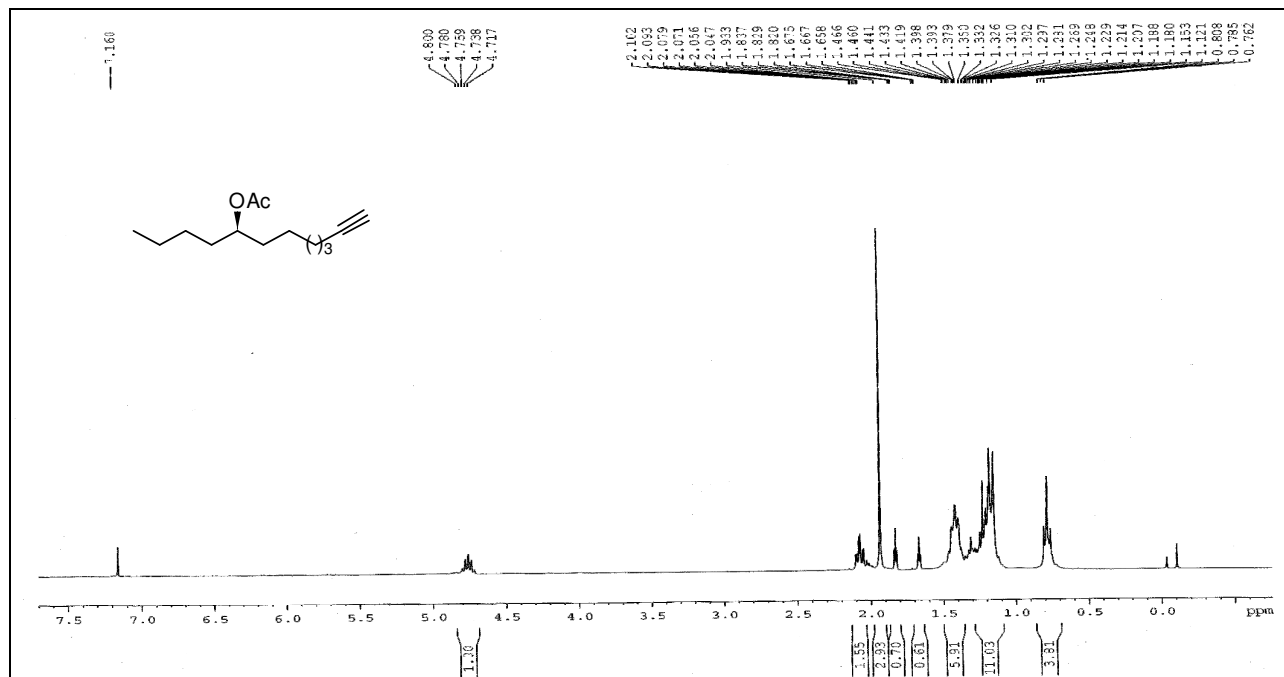
^1H NMR spectrum of 61b (300 MHz, CDCl_3):



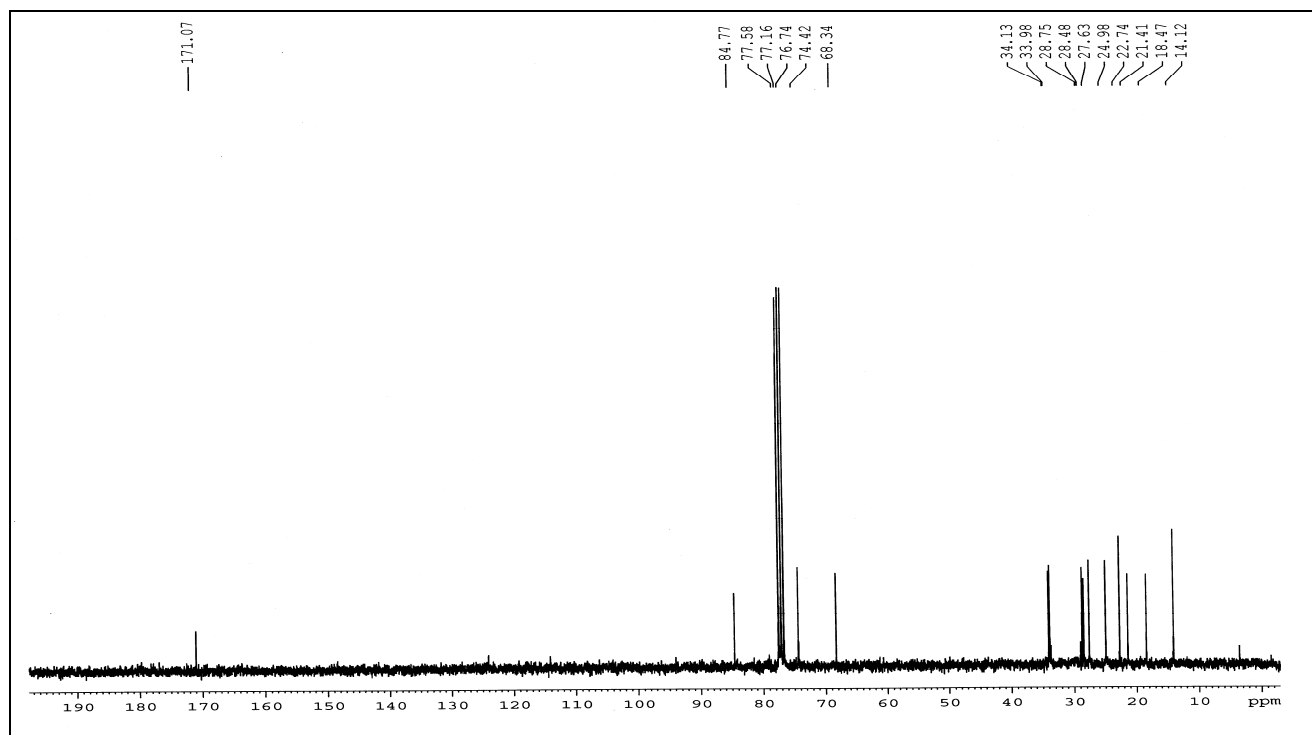
^{13}C NMR spectrum of 61b (75 MHz, CDCl_3):



^1H NMR spectrum of 62b (300 MHz, CDCl_3):



^{13}C NMR spectrum of 62b (75 MHz, CDCl_3):



Chemical structure of **63(a-d)** is shown above the spectrum. The structure is a complex molecule featuring a central core with two acetoxy (OAc) groups, a terminal alkyne, and a long alkyl chain with a terminal methyl group.

¹H NMR spectrum (CDCl₃) of compound **63(a-d)**. The x-axis represents the chemical shift in ppm, ranging from 0 to 8. The y-axis represents the intensity of the signal. The spectrum shows several distinct peaks, including a large peak at approximately 7.2 ppm (likely solvent or water), and a series of peaks between 0.5 and 2.5 ppm corresponding to the aliphatic protons of the molecule. Integration values are provided below the baseline for each major peak group.

Integration values (from left to right):

- 1.107
- 2.022
- 1.220
- 1.000
- 2.160
- 2.823
- 1.211
- 1.220
- 3.328
- 1.265
- 4.052
- 3.783
- 2.020
- 32.601
- 6.039
- 10.069
- 19.065
- 4.970

Chemical shift values (ppm) are listed on the right side of the spectrum:

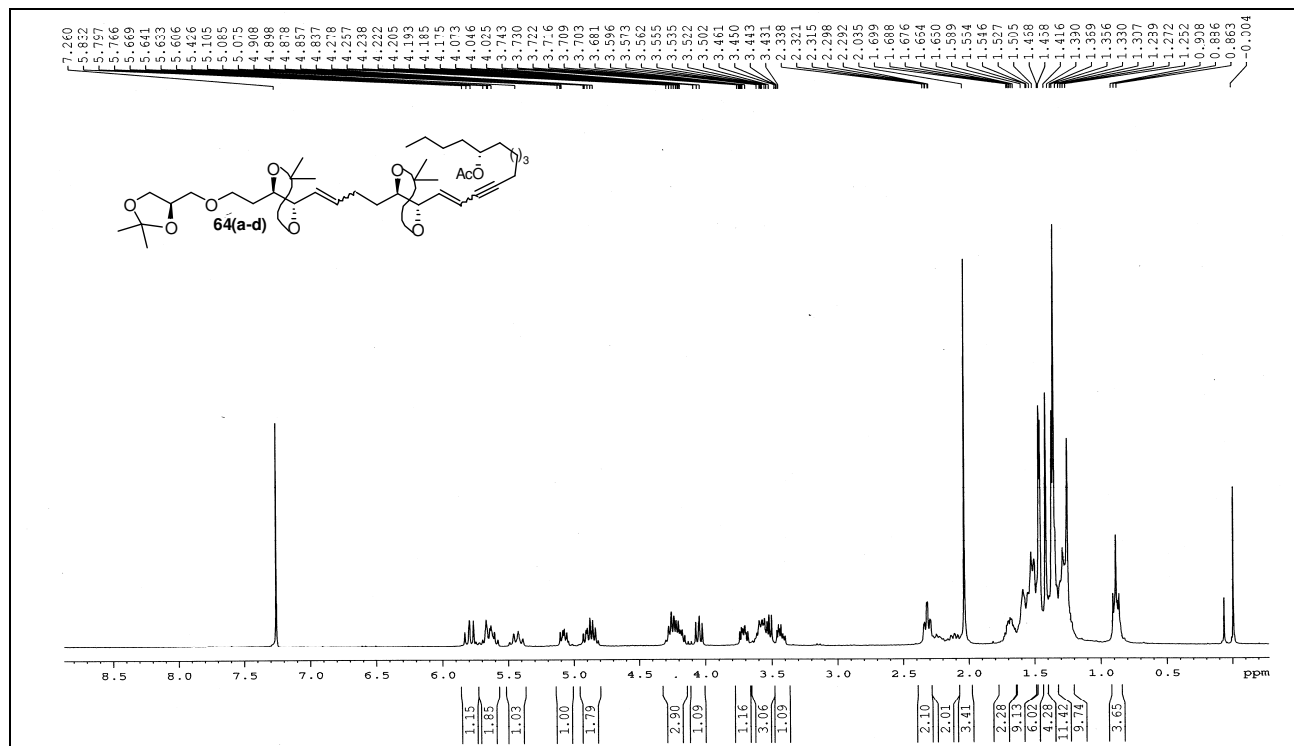
- 7.260, 5.850, 5.821, 5.814, 5.785, 5.681, 5.678, 5.649, 5.553, 5.522, 5.317, 5.160, 5.120, 5.112, 5.093, 4.877, 4.856, 4.835, 4.825, 4.274, 4.232, 4.221, 4.209, 4.202, 4.069, 4.048, 4.042, 3.921, 3.911, 3.733, 3.723, 3.717, 3.712, 3.706, 3.696, 3.603, 3.580, 3.556, 3.538, 3.523, 3.505, 3.450, 3.432, 3.412, 3.405, 3.408, 2.346, 2.339, 2.323, 2.315, 2.299, 2.289, 2.255, 2.232, 2.207, 2.037, 1.758, 1.736, 1.714, 1.666, 1.572, 1.520, 1.502, 1.473, 1.461, 1.424, 1.403, 1.384, 1.344, 1.332, 1.317, 1.292, 1.286, 1.283, 1.273, 1.244, 1.231, 0.970, 0.888, 0.865, -0.002.

Chemical shift values (ppm) labeled on the spectrum:

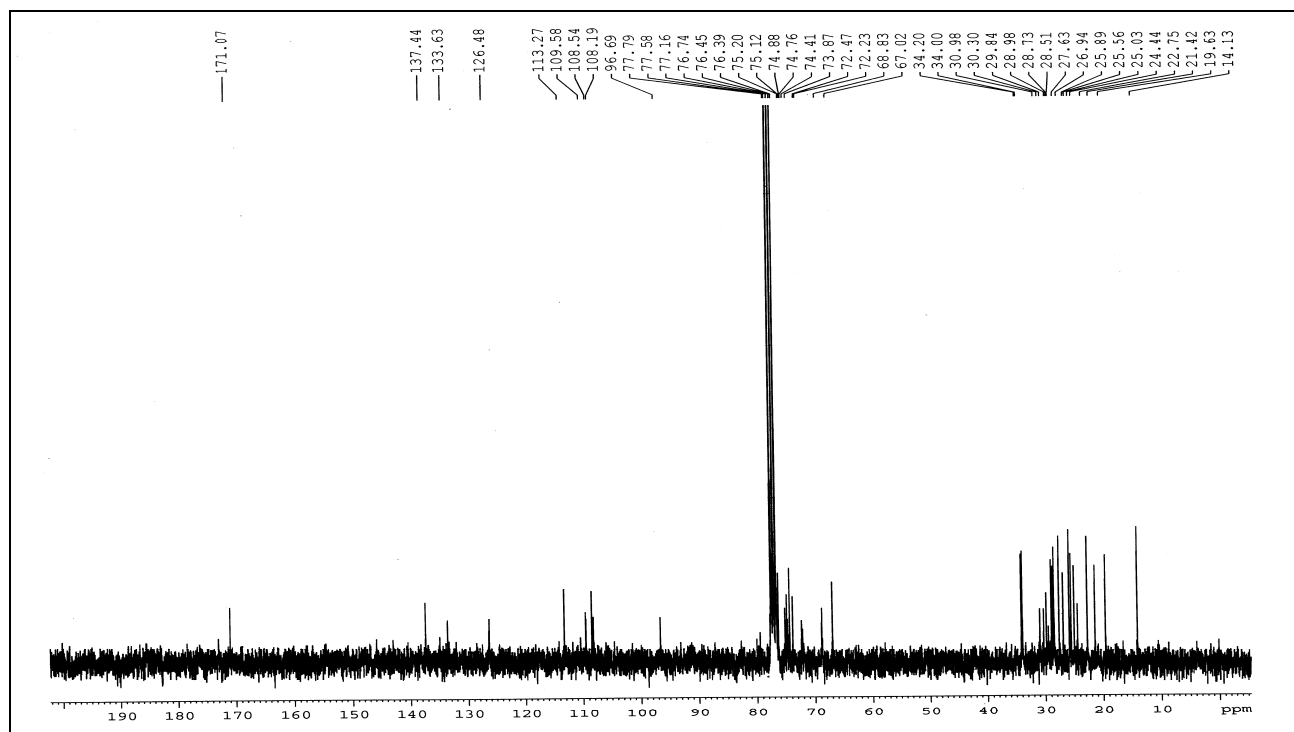
- 171.11
- 137.22
- 130.25
- 127.88
- 113.63
- 109.59
- 108.67
- 108.29
- 97.14
- 77.58
- 77.16
- 76.73
- 76.42
- 75.30
- 74.78
- 74.47
- 73.99
- 72.20
- 68.87
- 67.05
- 34.26
- 33.38
- 30.36
- 29.34
- 29.20
- 28.38
- 28.74
- 28.55
- 28.46
- 28.34
- 27.64
- 26.94
- 25.90
- 25.67
- 25.56
- 25.37
- 22.84
- 22.75
- 21.43
- 19.67

[illegible]

^1H NMR spectrum of 64 (a-d) (300 MHz, CDCl_3):



^{13}C NMR spectrum of 64 (a-d) (75 MHz, CDCl_3):



CC(C)(C)OC(=O)C[C@H](OCC1(C)C(C)C(C)C1)C[C@H](OCC2(C)C(C)C(C)C2)CCCCCCCC[C@H](OCC3(C)C(C)C(C)C3)C(=O)OCC

54

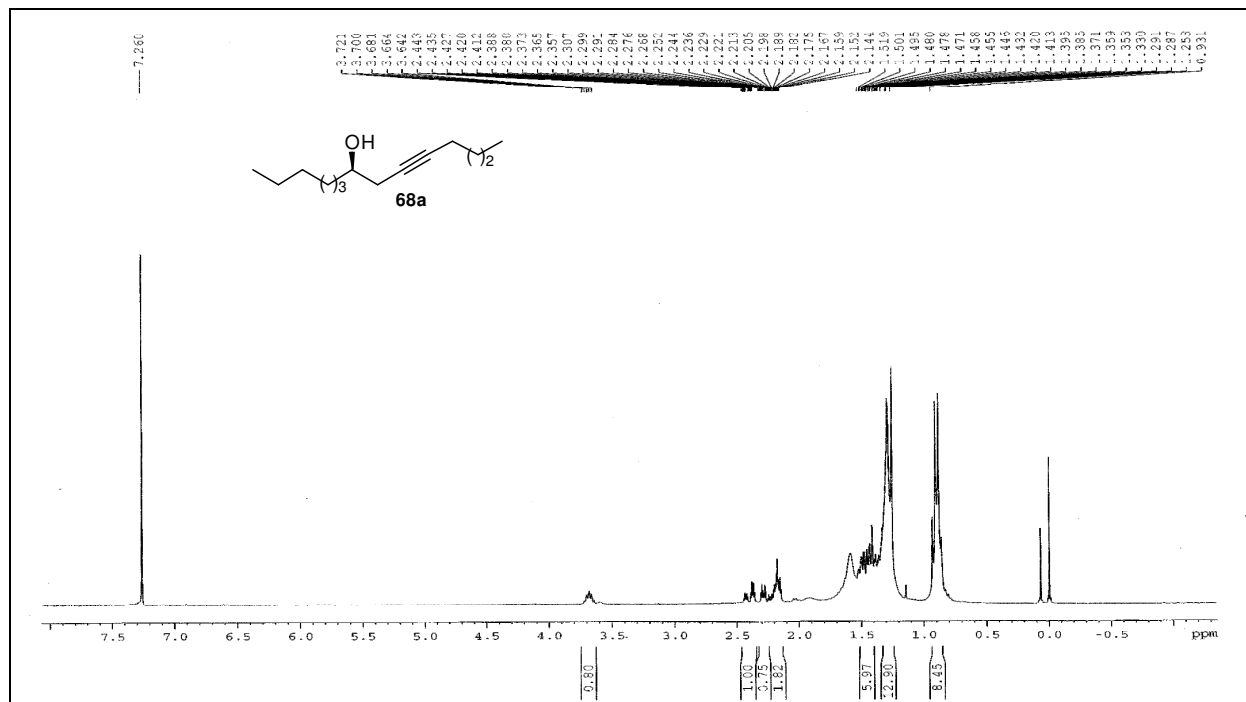
7.260
 4.854
 4.813
 4.813
 4.832
 4.811
 4.309
 4.304
 4.288
 4.248
 4.217
 4.228
 4.157
 4.117
 4.135
 4.100
 4.118
 4.135
 4.089
 4.075
 4.053
 4.047
 4.026
 3.997
 3.752
 3.731
 3.725
 3.709
 3.703
 3.682
 3.654
 3.633
 3.633
 3.619
 3.635
 3.595
 3.582
 3.570
 3.565
 3.550
 3.537
 3.522
 3.517
 3.521
 3.484
 3.464
 3.447
 3.432
 3.414
 2.034
 1.711
 1.711
 1.689
 1.665
 1.544
 1.518
 1.497
 1.477
 1.445
 1.420
 1.359
 1.327
 1.289
 1.280
 1.252

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

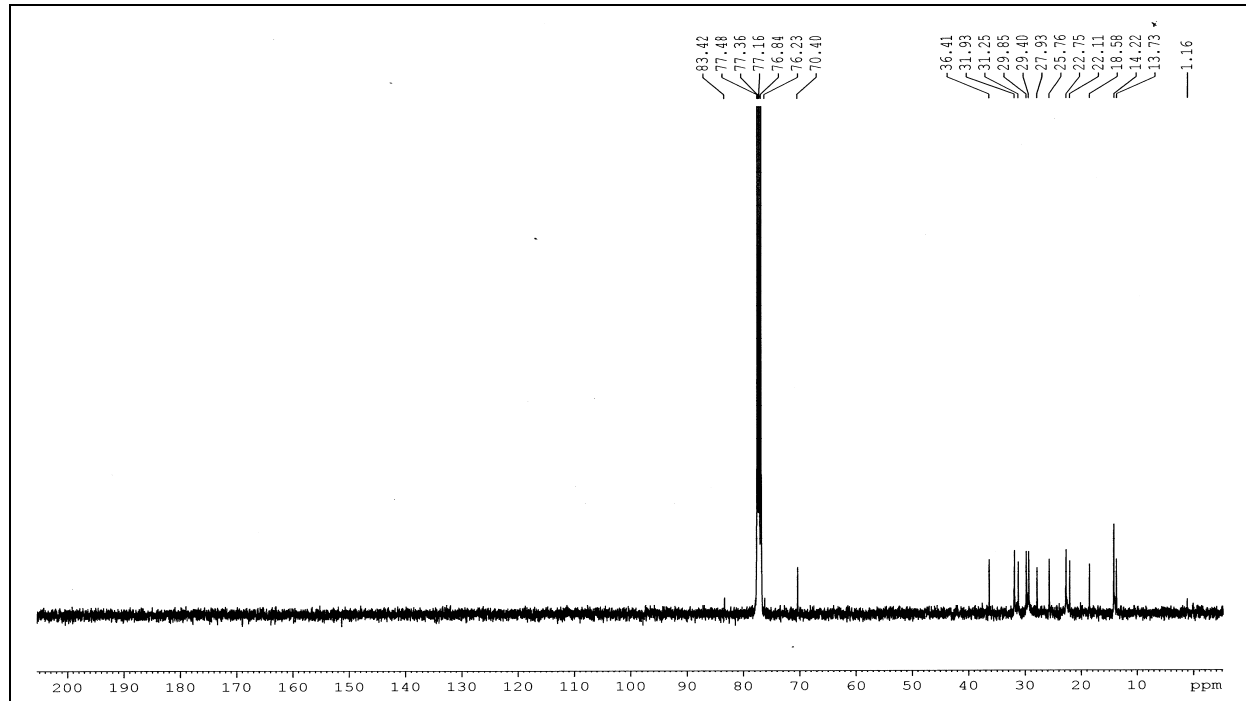
1.00
 0.96
 0.90
 3.26
 1.20
 7.71
 0.95
 3.00
 3.04
 9.66
 8.88
 30.52
 3.32

¹³C NMR spectrum (CDCl₃) of compound 10. The x-axis represents chemical shift in ppm, ranging from 180 to 0. The spectrum shows a carbonyl peak at 171.10 ppm, aromatic peaks at 109.60, 107.67, and 107.44 ppm, a solvent peak at 77.16 ppm, and aliphatic peaks at 78.41, 78.13, 77.99, 77.59, 76.74, 74.51, 74.61, 74.59, 72.42, 68.43, 66.98, 34.29, 33.98, 33.88, 30.33, 29.65, 29.70, 29.68, 28.61, 27.64, 26.94, 26.56, 26.42, 26.17, 25.57, 25.48, 22.76, 21.45, and 14.14 ppm.

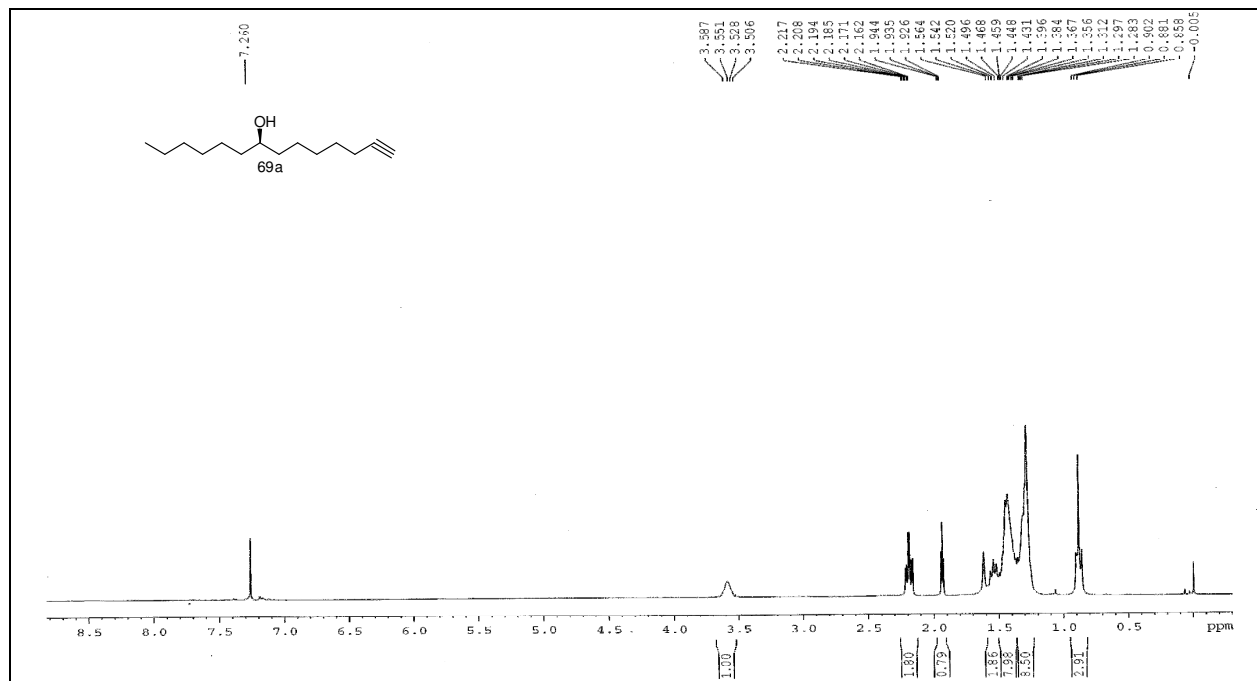
^1H NMR spectrum of 68a (300 MHz, CDCl_3):



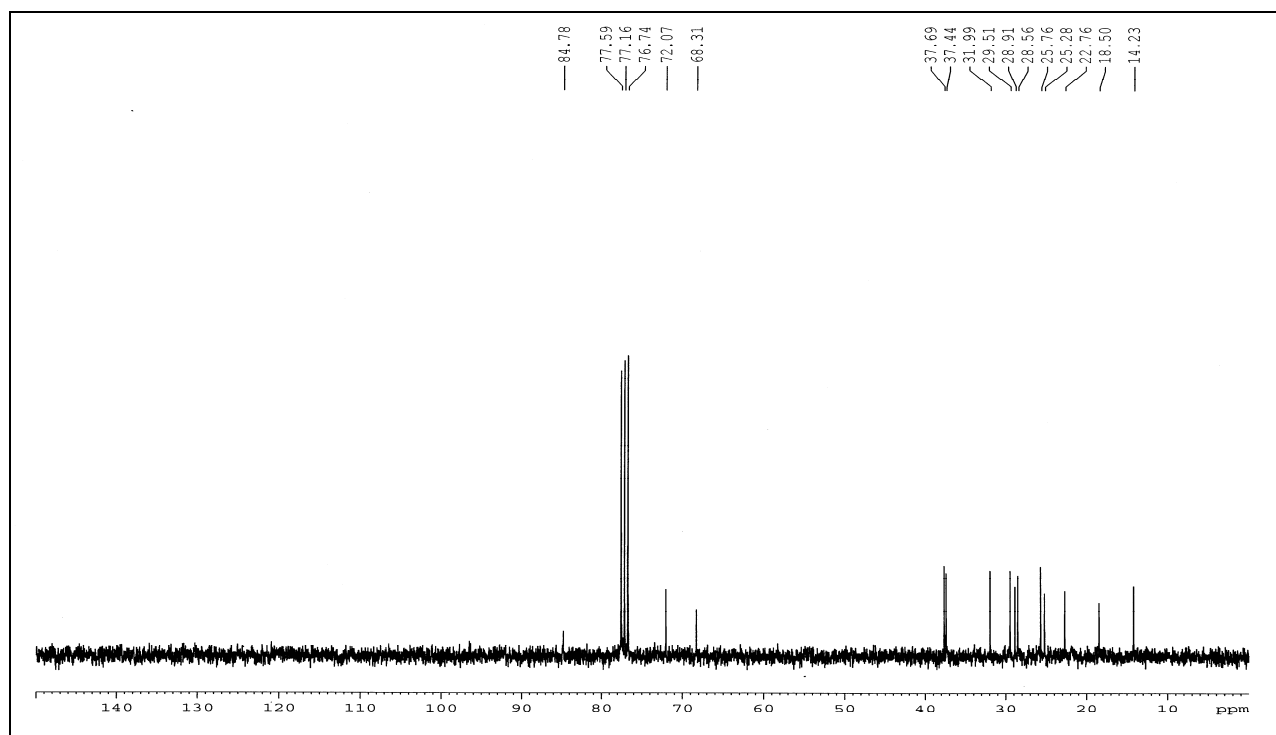
^{13}C NMR spectrum of 68a (75 MHz, CDCl_3):



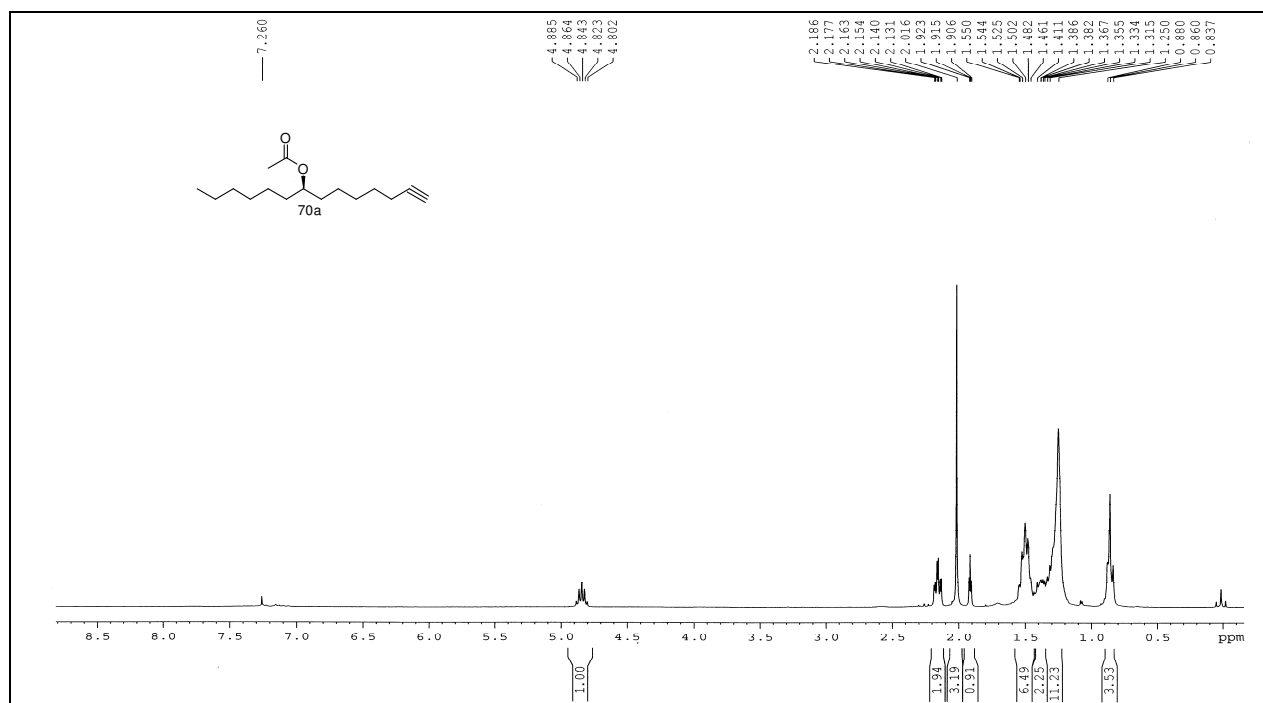
^1H NMR spectrum of 69a (300 MHz, CDCl_3):



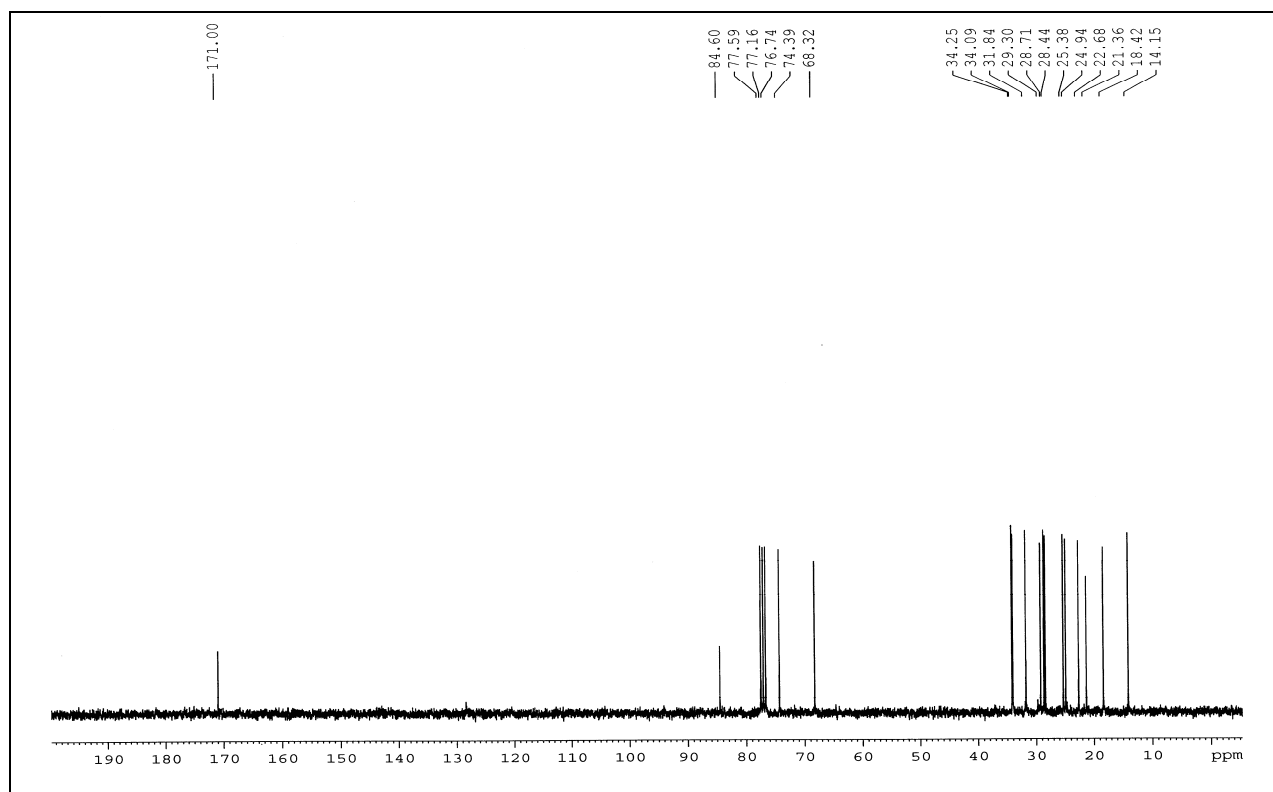
^{13}C NMR spectrum of 69a (75 MHz, CDCl_3):



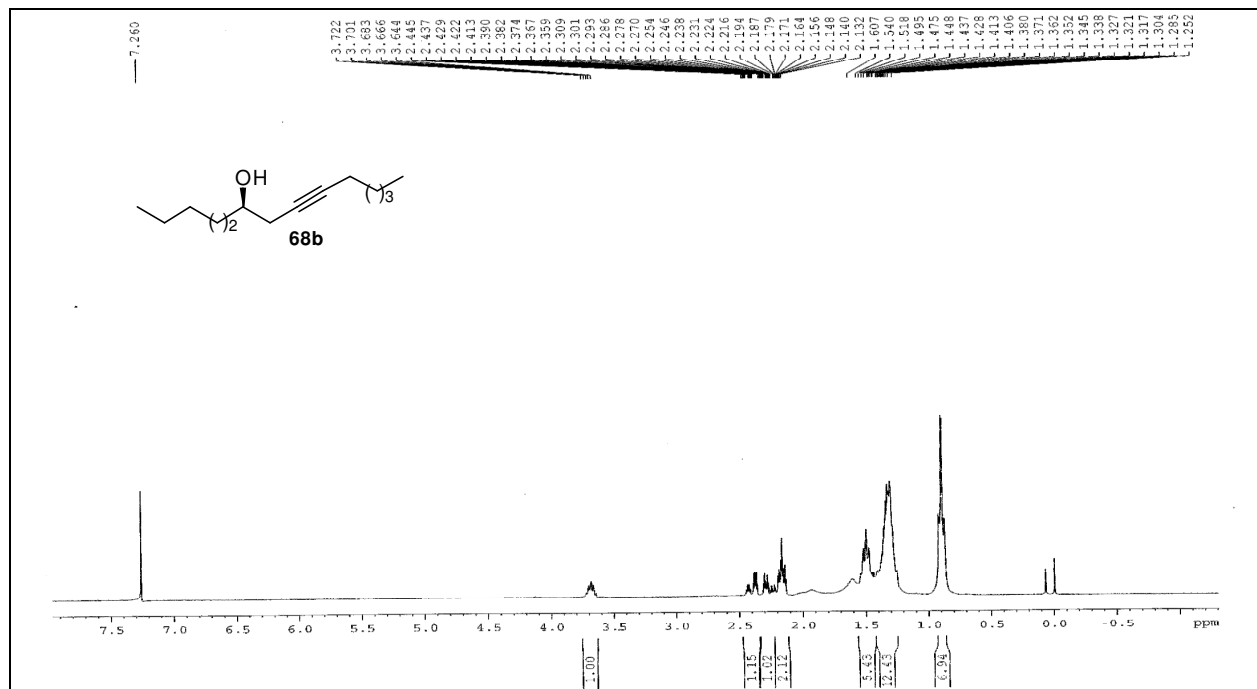
^1H NMR spectrum of 70a (300 MHz, CDCl_3):



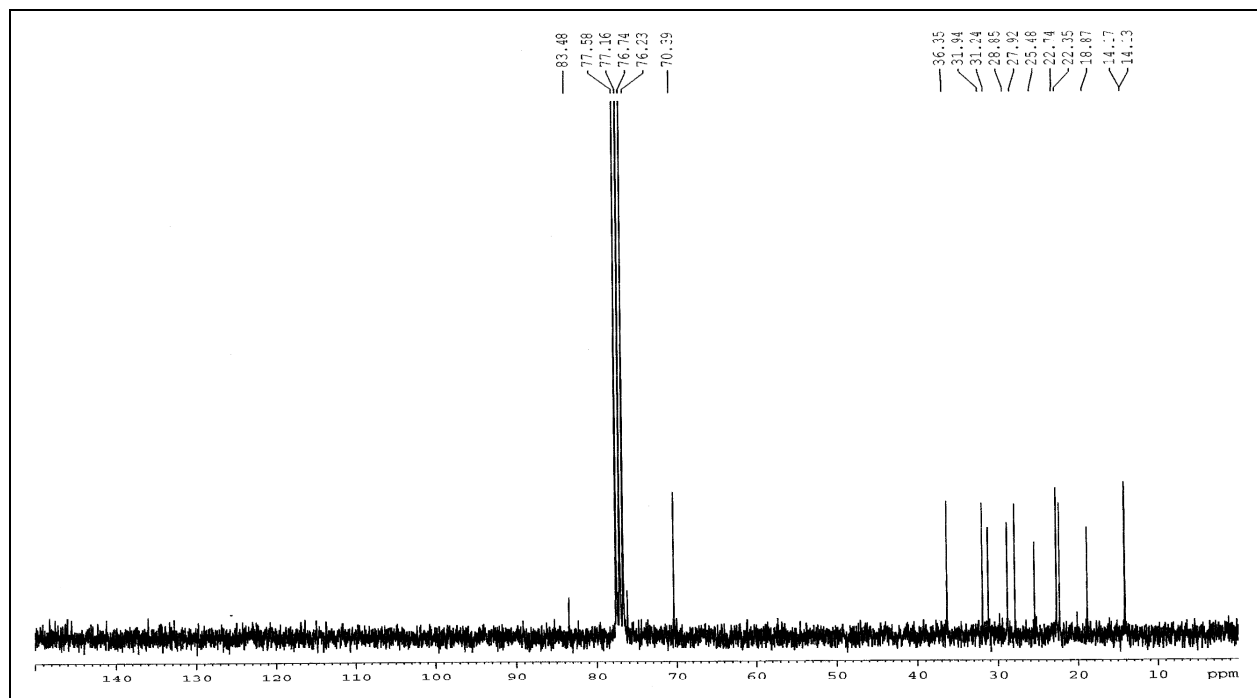
^{13}C NMR spectrum of 70a (75 MHz, CDCl_3):



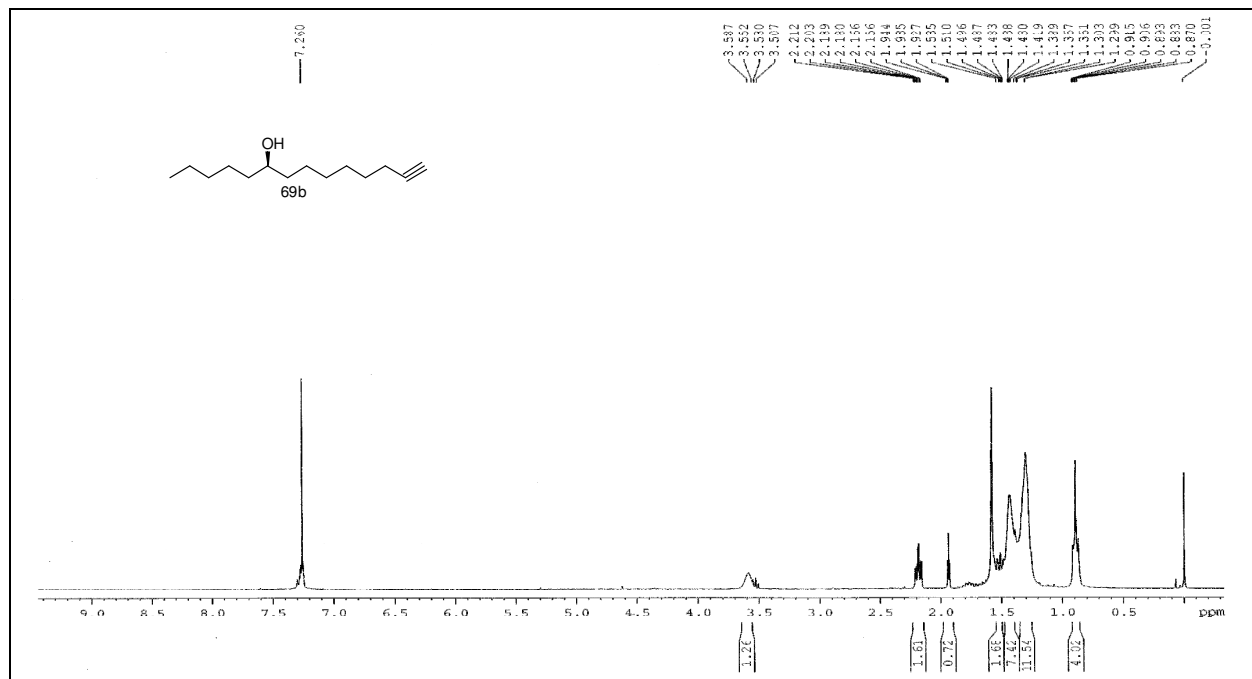
^1H NMR spectrum of 68b (300 MHz, CDCl_3):



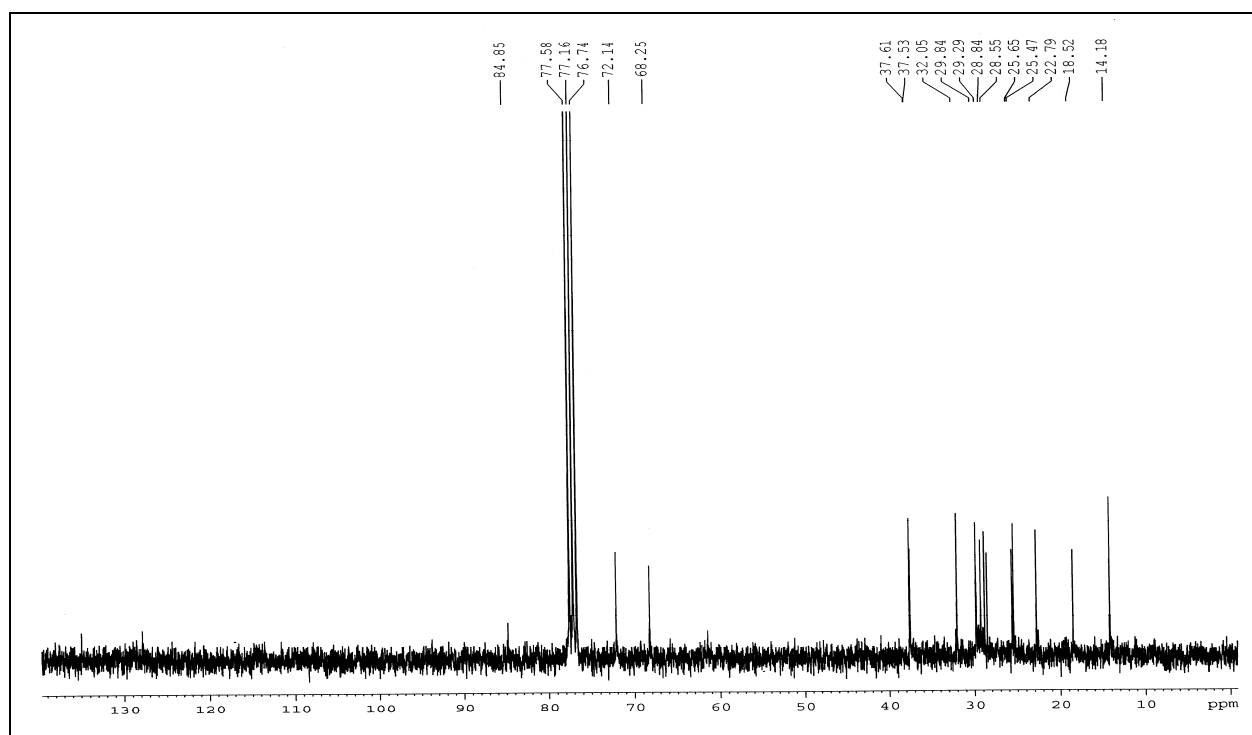
^{13}C NMR spectrum of 68b (75 MHz, CDCl_3):



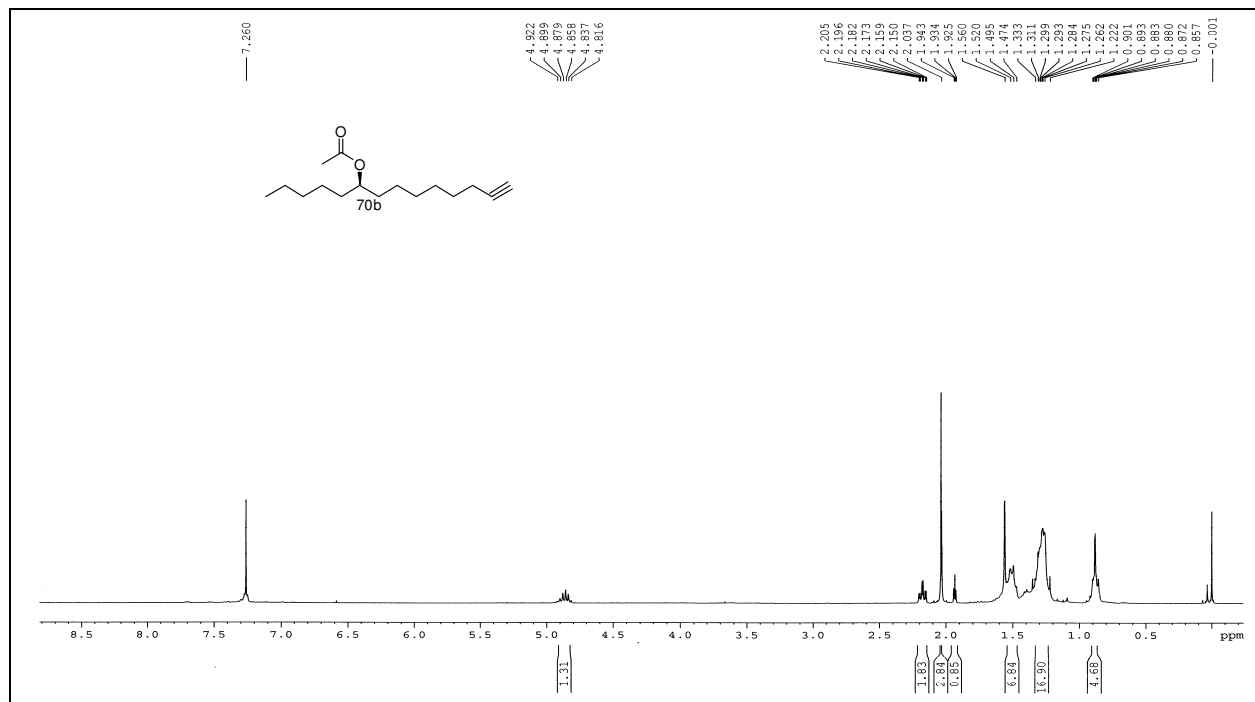
^1H NMR spectrum of 69b (300 MHz, CDCl_3):



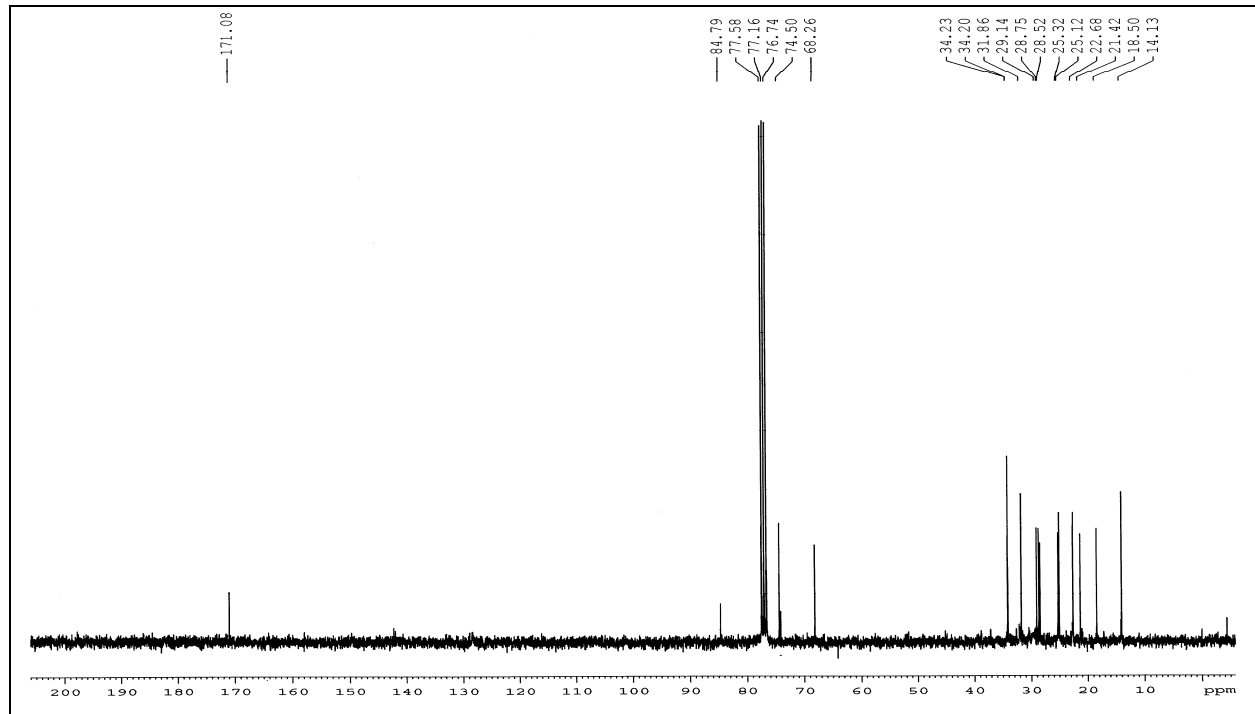
^{13}C NMR spectrum of 69b (75 MHz, CDCl_3):



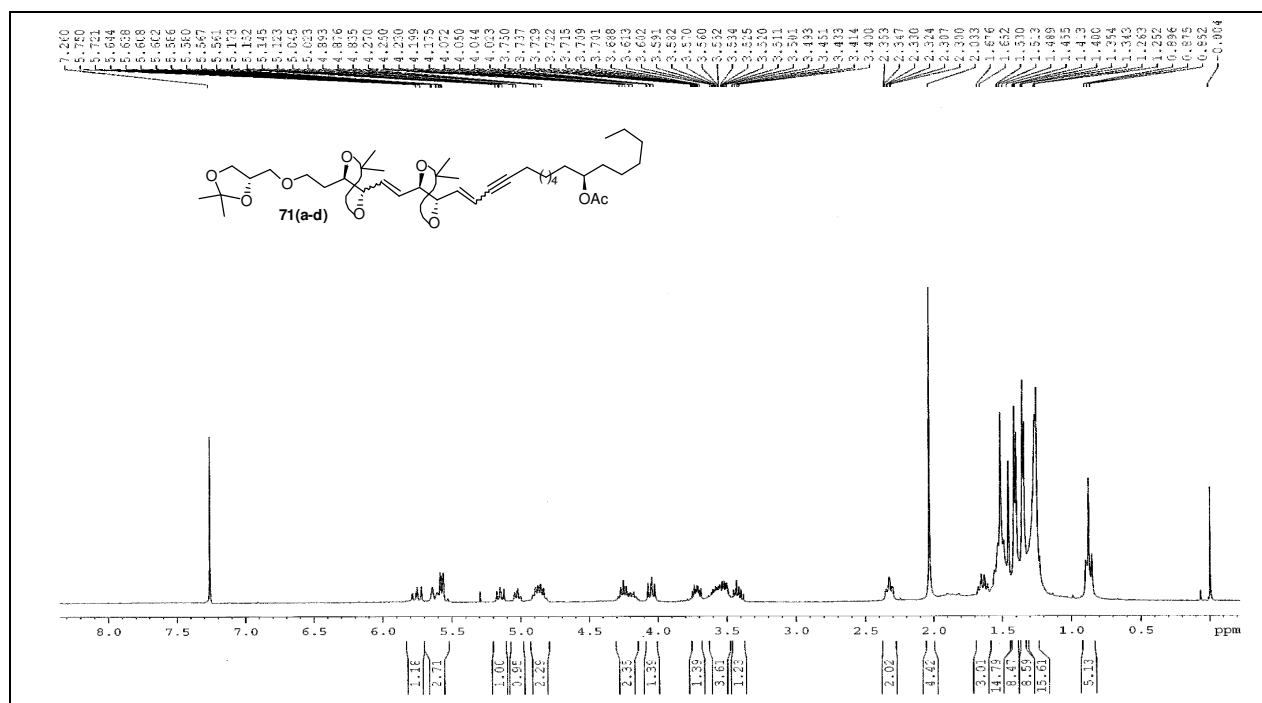
^1H NMR spectrum of 70b (300 MHz, CDCl_3):



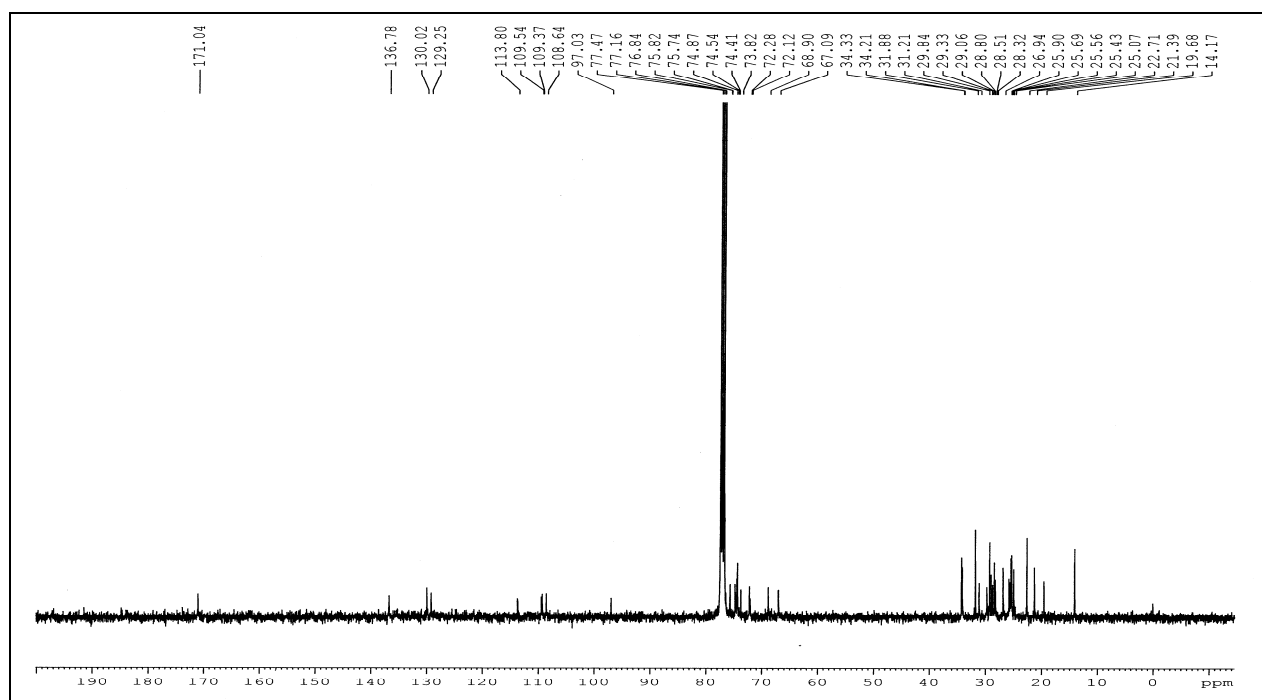
^{13}C NMR spectrum of 70b (75 MHz, CDCl_3):



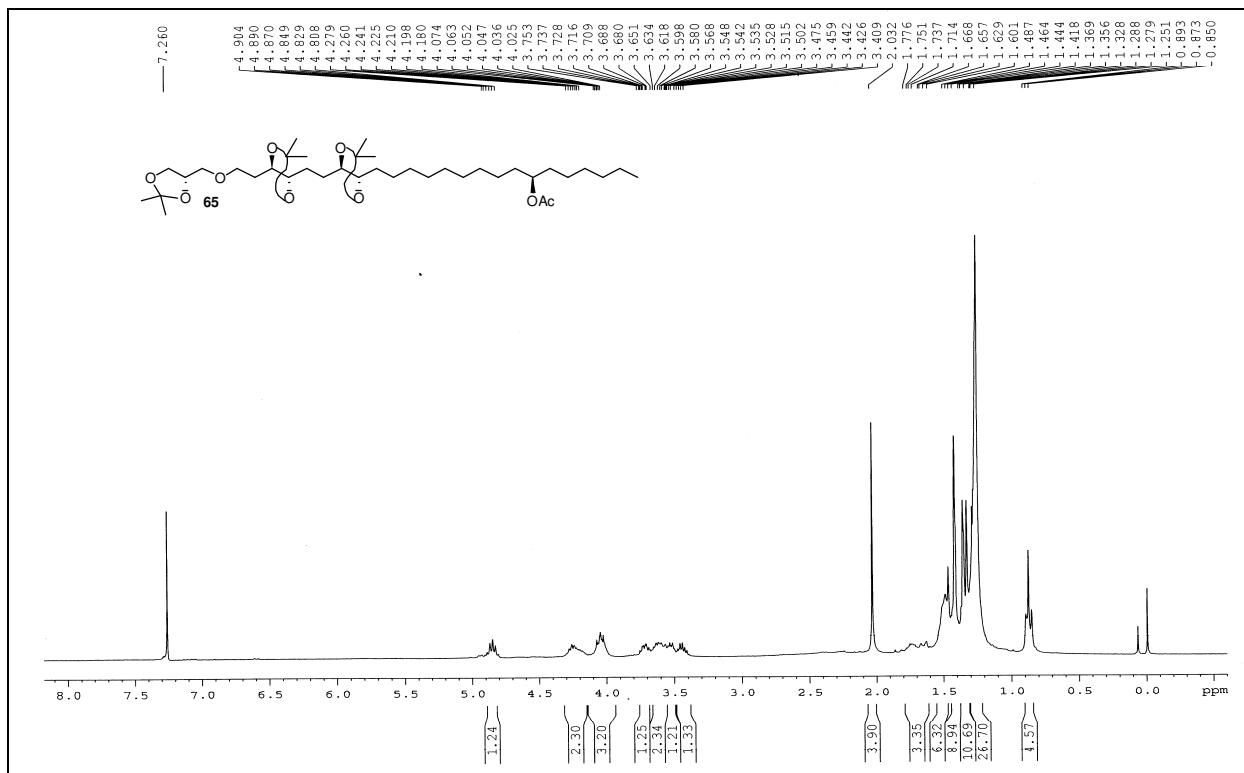
¹H NMR spectrum of 71 (a-d) (300 MHz, CDCl₃):



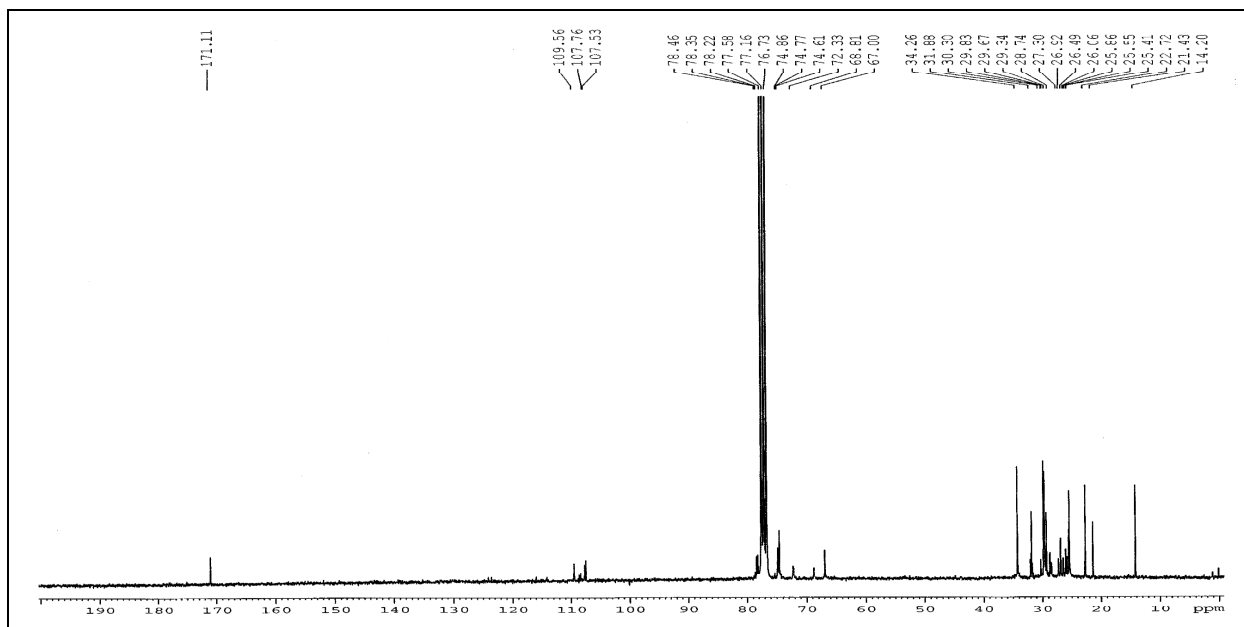
^{13}C NMR spectrum of 71 (a-d) (75 MHz, CDCl_3):



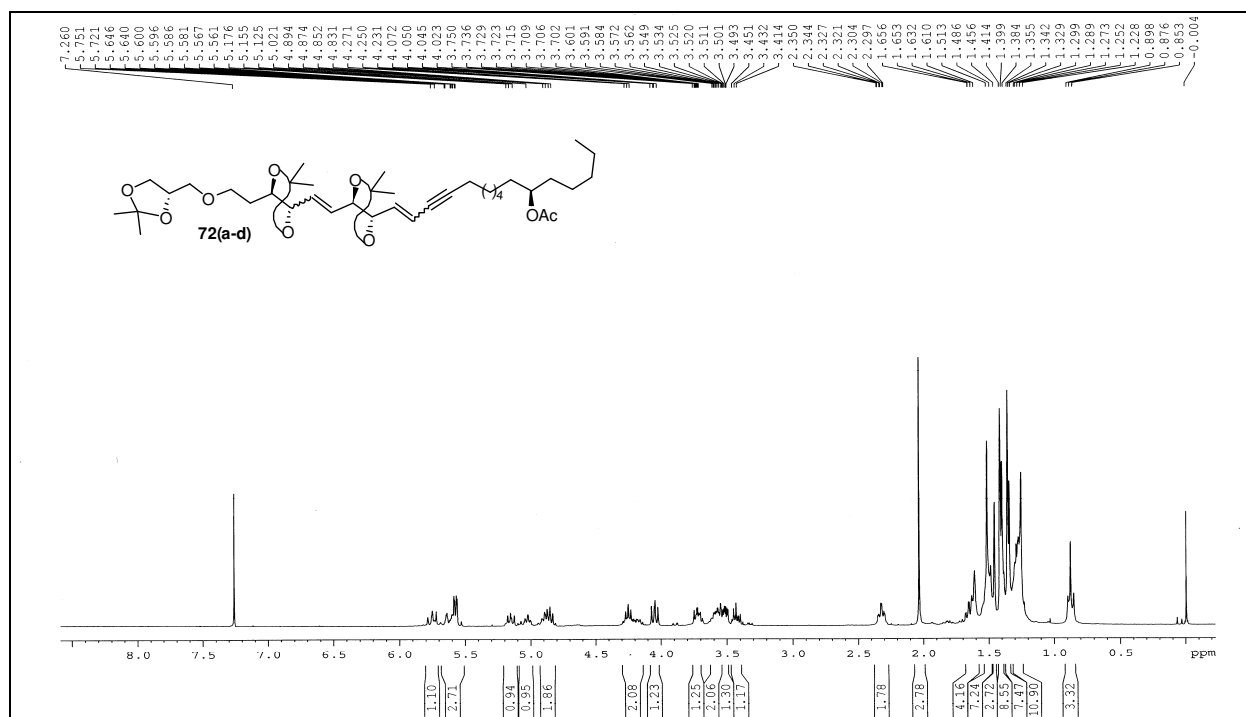
^1H NMR spectrum of 65 (300 MHz, CDCl_3):



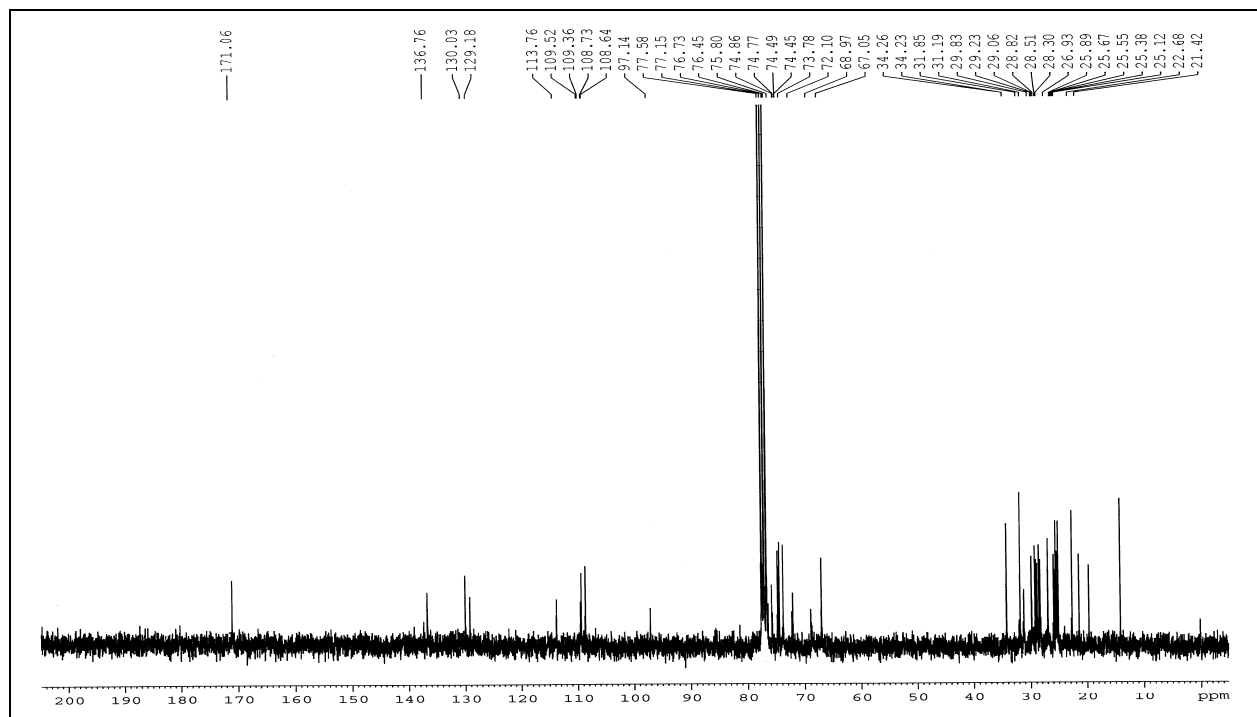
^{13}C NMR spectrum of 65 (75 MHz, CDCl_3):



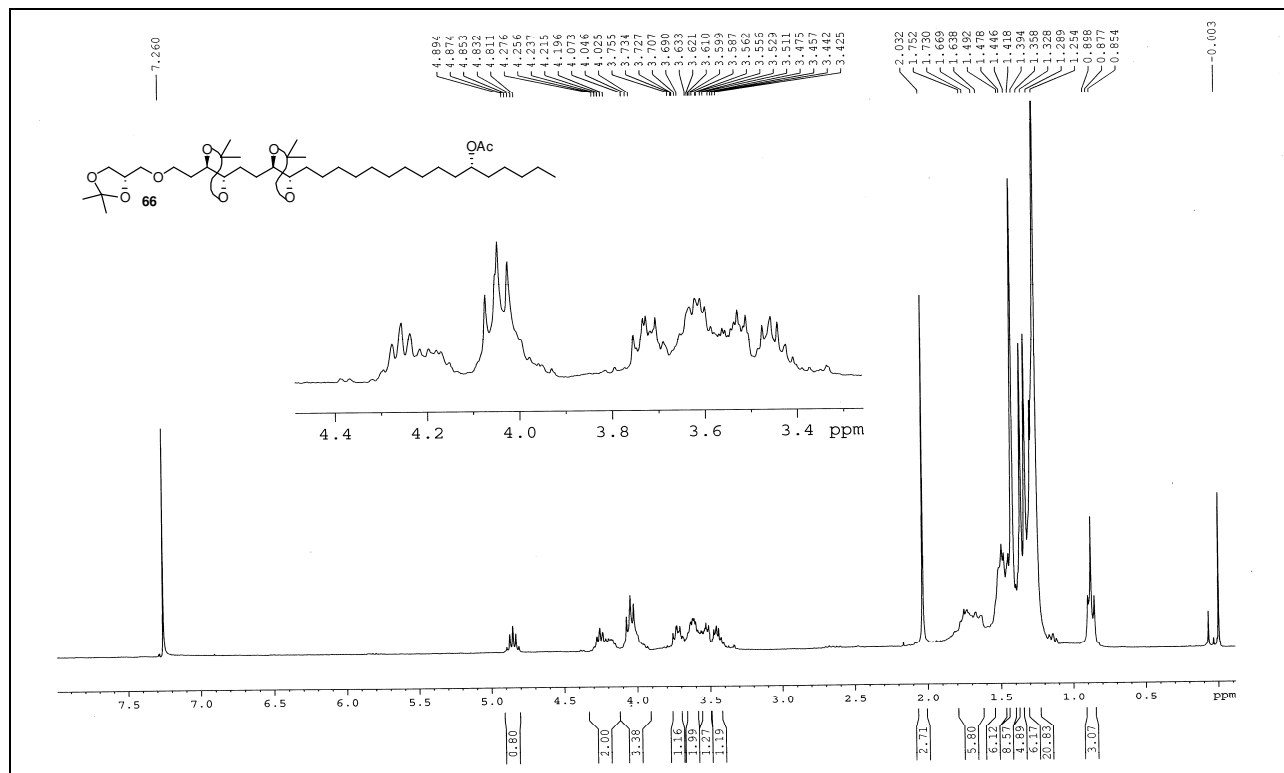
^1H NMR spectrum of 72 (a-d) (300 MHz, CDCl_3):



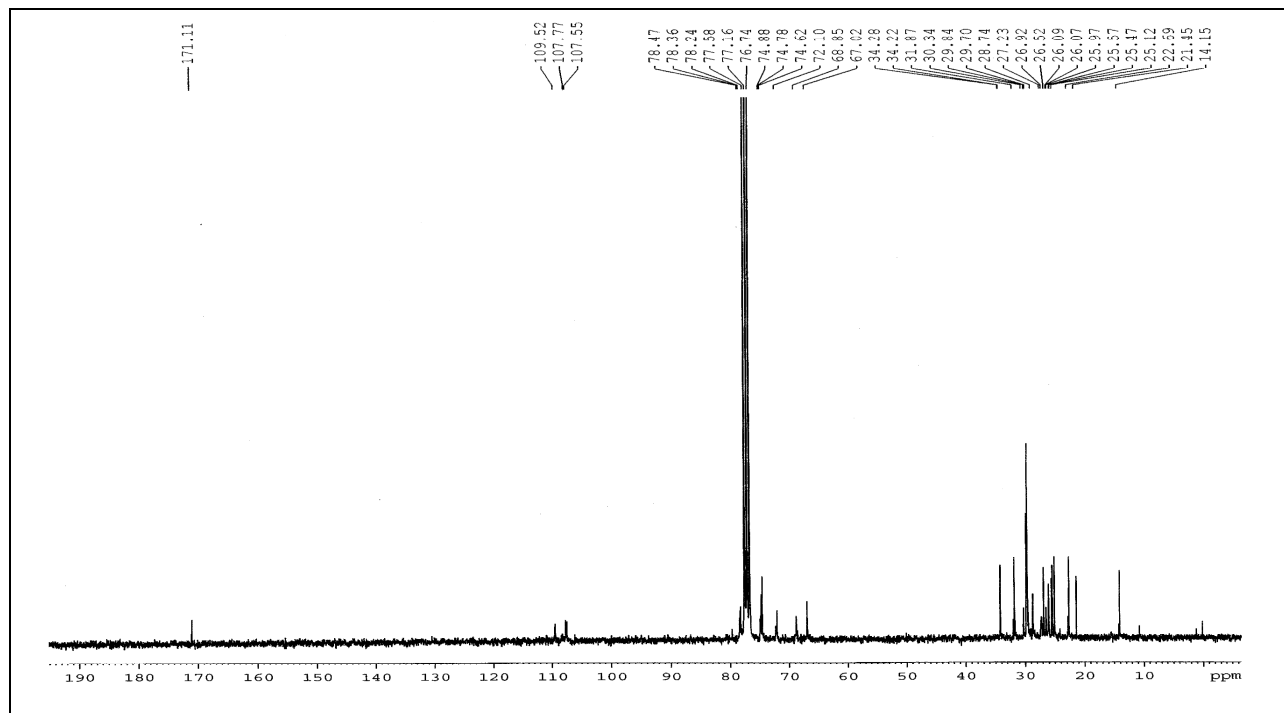
^{13}C NMR spectrum of 72 (a-d) (75 MHz, CDCl_3):



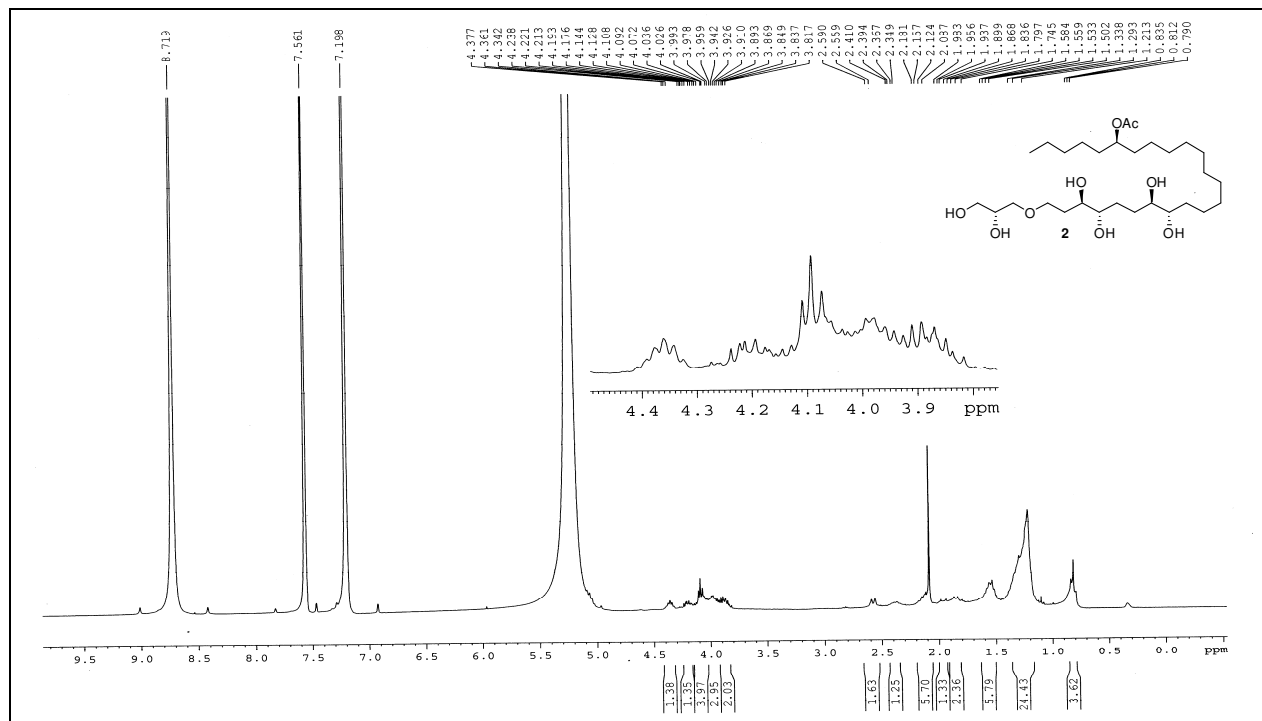
^1H NMR spectrum of 66 (300 MHz, CDCl_3):



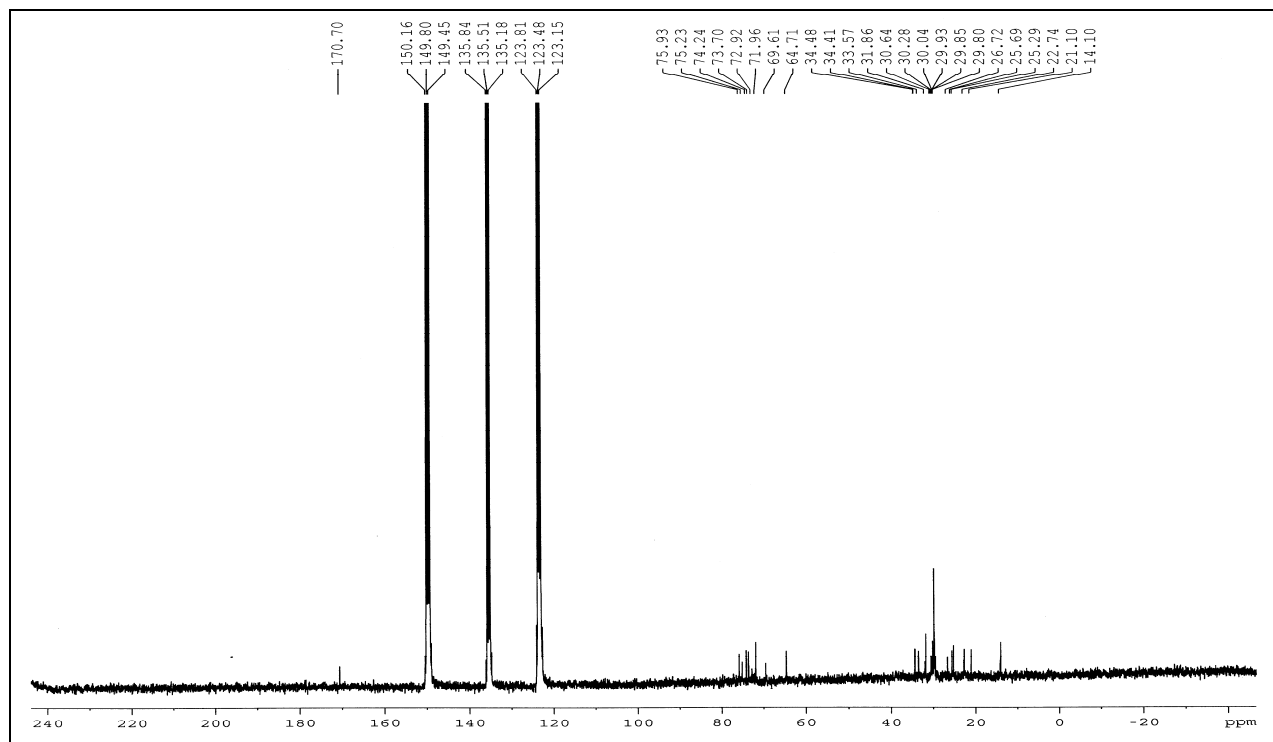
^{13}C NMR spectrum of 66 (75 MHz, CDCl_3):



^1H NMR spectrum of 2 (300 MHz, $\text{C}_5\text{D}_5\text{N}$):



^{13}C NMR spectrum of 2 (75 MHz, $\text{C}_5\text{D}_5\text{N}$):



HRMS spectrum of 2:

